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Presented by: BARA Imene, KERROUM Raghed

Contribution to the study of the dye effect on the conversion efficiency of DSSCs

Presented on 07 / 07 / 2020,, Infront of the committee

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Dedication:

To The sake of Allah, my Creator and my Master, my great teacher and messenger, Mohammed (peace be open him), who taught us the purpose of life.

To my dearest parents, ***Ahmed*** *and* ***Aisha*** *to whom my gratitude and appreciation could never be expressed, for never stopping to give of themselves in countless ways, for making me the person I am today.*

May god protect them.

To my Brothers, my uncle, my aunts, cousins and many friends.

To ***Imene****, whom I am extremely proud of and grateful for.*

I dedicate this research.

RAGHED Kerroum

Dedication:

I thank almighty God for the courage and strength that he has given me to finish this work,

*To my mother **Zohra** and my father **Mohammed**, who have never stopped praying for me and encouging me, may God protect them,*

*To my whole family, from the biggest to the smallest. To my sisters **Safa** and **Fethia**, to my brothers **Nabil** and **Abd latif.***

*To my friends, **Achref, Sawsen, Khadidja**, **Houssem** and **Imad.***

*To **Raghed***

You have worked hard for me without counting the cost, in recognition of all the sacrifices made by each and every one of you to enable me to reach this stage of my life. With all my tenderness.

I dedicate this manuscript.

Imene BARA.

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We did not inherit this world from our parents. . . .
We are borrowing it from our children.
(Author unknown) Earth is what we all have in common,
We hope that this manuscript is helpful to students, researchers and engineers,
Who are willing to take part in the creation of a safe world for the future generations.

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Abstract:

Dye-sensitized solar cells (DSSCs) have attracted significant attention as alternatives to conventional silicon-based solar cells owing to their low-cost production, facile fabrication, excellent stability and high-power conversion efficiency (PCE). The dye molecule is one of the Key components in DSSCs since its significant influence on the PCE, charge separation, Light-harvesting, as well as the device stability. Among various dyes, easily tunable Phenothiazine-based dyes hold a large proportion and achieve impressive photovoltaic performances. This class of dyes possesses excellent electron donating ability. This manuscript summarized a development of a QSPR model that can predict the power conversion efficiency of new sensitizers using molecular structures from phenothiazine family.

The model established shows promising results and can be used as tool to test the efficiency of new dyes and then passing to the experimental step if good results are obtained.

Key words: **Organic Dyes; Solar Cells; QSPR modeling; DSSCs; Renewable Energy**

Résumé :

Les cellules solaires sensibilisées aux colorants (DSSC) ont attiré une grande attention en tant qu'alternatives aux cellules solaires conventionnelles à base de silicium en raison de leur faible coût de production et de leur facilité de fabrication, une excellente stabilité et un rendement élevé de conversion de puissance (PCE). La molécule de colorant est l'une des Composants clés des DSSC depuis son influence significative sur l'ECP, la séparation des charges, La récolte de la lumière, ainsi que la stabilité du dispositif. Parmi les différents colorants, facilement accordable Les colorants à base de phénothiazine en contiennent une grande partie et permettent d'obtenir des résultats impressionnants en matière de photovoltaïque performances. Cette classe de colorants possède une excellente capacité à donner des électrons. Cette thèse résumé les développements d'un modèle QSPR qui peut prédire l'efficacité de conversion de puissance de nouveaux sensibilisants en utilisant des structures moléculaires de la famille des phénothiazines. Le modèle établi montre des résultats prometteurs et peut être utilisé comme outil pour tester l'efficacité de nouveaux colorants et passer ensuite à l'étape expérimentale si de bons résultats sont obtenus.

Mots clés : **Colorants organiques, cellules solaire, modélisation QSPR, DSSCs, énergie renouvelable**

ملخص

اجتذبت الخلايا الشمسية الحساسة للصبغة (DSSCs) اهتمامًا كبيرًا كبدائل للخلايا الشمسية التقليدية القائمة على السيليكون نظرًا لإنتاجها منخفض التكلفة، وتصنيعها بالسطح، والاستقرار الممتاز، وكفاءة التحويل العالية للطاقة (PCE). جزيء الصبغة هو أحد المكونات الرئيسية في DSSCs منذ تأثيره الكبير علىPCE ، وفصل الشحن، وحصاد الضوء، وكذلك استقرار الجهاز. من بين الأصباغ المختلفة، تحتوي الأصباغ القائمة على الفينوثيازين القابلة للضبط بسهولة على نسبة كبيرة وتحقق أداء ضوئيًا مثيرًا للإعجاب. تمتلك هذه الفئة من الأصباغ قدرة ممتازة على التبرع بالإلكترونات. لخصت هذه الأطروحة تطور نموذج QSPR الذي يمكن أن يتنبأ بكفاءة تحويل الطاقة من أجهزة التحسس الجديدة باستخدام الهياكل الجزيئية من عائلة الفينوثيازين.

يوضح النموذج الذي تم إنشاؤه نتائج واعدة ويمكن استخدامه كأداة لاختبار كفاءة الأصباغ الجديدة ثم الانتقال إلى الخطوة التجريبية إذا تم الحصول على نتائج جيدة.

GENERAL INTRODUCTION

General introduction

Today, satisfaction of the world's energy needs is mainly based on fossil resources, as well as, on nuclear power. Using these resources for energy generation produces tons of carbon dioxide that promote the greenhouse effect and the climate change. Though the emission of nuclear power plants is lower, the generation of electricity comes along with the production and the problem of storing high-level radioactive waste. Furthermore, safety concerns arise through severe nuclear power plant accidents. These issues demand for a transition to alternative, renewable, environmentally friendly, and safer sources of energy [1]. In this context, photovoltaic energy appears as an interesting alternative. Today, 99% of photovoltaic cells are silicon-based. At the very same time, other technologies based on organic materials are tending to develop to solve the problem of production costs in particular. Organic dye sensitized solar cells are a relatively recent field since they emerged in the 1990s, and has experienced strong development especially since the early 2000s with successful scientific and technological advances. DSSCs have two main advantages over the silicon industry which are likely low production costs with simple manufacturing procedures, and a potentially wider field of application due to their flexibility and lightness. DSSCs represent a highly multidisciplinary field requiring advanced skills in molecular and macromolecular engineering, physical chemistry and materials physics. Energy conversion efficiencies can be improved by working upstream on understanding the chemical and physico-chemical mechanisms involved in active materials and on the technological aspects of photovoltaic devices.

Recently, the molecular design of organic dyes using quantum chemical calculations has been adopted, leading to great achievements. Quantum chemical methods can capture the physical essence of molecular systems, and machine learning methods can explore the central relationship between molecular structures and the target properties or observed activities through the quantum chemical molecular descriptors. As a result, applying quantum chemical methods together with machine learning methods to investigate the quantitative structure–property relationship (QSPR) of all-organic dyes in DSSCs. With the QSPR model, the power conversion efficiency (PCE) of new organic dye sensitizers can be predicted, which cannot only save numerous resources but also provide some guidance for the synthesis of highly efficient dye sensitizers [2].

In this respect, it is in this context that our manuscript flows. The objective is the development of a predictive model represented by an equation for the power conversion efficiency of dye sensitized solar cells, this model is based on elaborating a relationship between the power conversion efficiencies from the database and the different properties of the studied dyes.

Elaborating this kind of model offers to scientists and the industrial society of this field a great opportunity to save money and time by only choosing the tested dyes that give the best results and then use it to produce a high-power conversion efficiency cells.

To this end, the manuscript is structured in four detailed chapters as follows:

A first introductory chapter is the presentation of photovoltaic solar cells with its different types, parameters, operating principle and also the environmental impact of using photovoltaic energy as an alternative of fossil fuel resources.

In the second chapter, the main compounds of organic dye sensitized solar cells and its functioning will be detailed. Then a comparison between organic and inorganic solar cells will be developed, in addition, major DSSC’s limitations and difficulties to overcome will be mentioned.

A third chapter all about QSPR modeling and quantum chemical methods will be introduced, a brief definition of QSPR modeling, its use for DSSCs and the most important methods of quantum chemicals used in this manuscript will be mentioned.

The last chapter will be dedicated to the predictive model established using the MOE software (molecular operating environment), the quantum chemical methods chosen to build the model will be mentioned and the simulation of results and discussions will be presented.

Finally, a general conclusion crowns this manuscript to summarize our analyses, results and comments.

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[2]: Hongzhi Li, Ziyan Zhong, Lin Li, Rui Gao, Jingxia Cui, Ting Gao, Li Hong Hu,Yinghua Lu, Zhong-Min Su, Hui Li, A Cascaded QSAR Model for Efficient Prediction of Overall Power

Chapter I : GENERALITIES

I. INTRODUCTION

Solar energy is the portion of the Sun’s radiant heat and light, which is available at the Earth’s surface for various applications of generating energy, that is, converting the energy form of the Sun into energy for useful applications. This is done, for example, by excited electrons in a photovoltaic cell, or by heating objects. This energy is free, clean, and abundant throughout the year and is important especially at the time of high fossil fuel costs and degradation of the atmosphere by the use of these fossil fuels. Solar energy is carried on the solar radiation [1]. This energy is the most dominant of all renewable energies, it is the origin of the energy sources used by man (in chemical and biochemical form in particular). Thanks to it, it is now possible to produce Electricity by using photovoltaic (PV) panels.

Initially, photovoltaic electricity was developed for stand-alone applications without connection to a power grid, mainly for the supply of isolated consumers (not connected to a grid) with an installed power ranging from a few tens to a few hundred Watts. Now; it can be found in applications of various powers. This evolution has been made possible thanks to continuous research and development over the last few years, but also through the improvement of various techniques, methods and devices.

Photovoltaic (PV) technology converts solar energy into electrical energy using semiconductors. This is the technology with the greatest potential, but also the one that requires the most of technical development. This technology is the basis for photovoltaic solar cells which have seriously started to be developed and studied since the 1950s when the first silicon-based solar cell crystalline, with a yield of 6%, was developed in Bell Laboratories.0

Optimization of the performance of photovoltaic and other systems that convert sunlight into other useful forms of energy is contingent on knowledge of the properties of sunlight and photovoltaic systems. In order to best accomplish our study, we introduced this chapter with a short presentation and some generalities on solar radiation and photovoltaics. This chapter provides a synopsis of important solar phenomena, and will emphasize the characteristics of PV system.

II. INTRODUCTION TO SOLAR ENERGY

II. 1. Solar radiation

Any discussion of solar energy and solar (photovoltaic) cells should begin with an examination of the energy source, the sun. The sun has a mass of approximately 1024 tons, a diameter of 865,000 miles, and radiates energy at a rate of some 3.8 x 1020 megawatts. Present theories predict that this output will continue, essentially unchanged, for several billion years. [2]

To maintain life in our solar system, energy is needed. The earth receives this energy from the sun, which is about 5000 [3] times the input to the Earth's energy budget from all other sources; this means that in one hour our planet obtains enough energy to meet the needs of nearly a year. In order to maximize the utilization of this important energy resource, it is advantageous to understand some of the properties of the sun.

The sun is composed of a mixture of gases with a predominance of hydrogen. The source of solar energy are the nuclear interactions at the core of the Sun. As the sun converts hydrogen to helium in a massive thermonuclear fusion reaction, mass is converted to energy according to Einstein's famous formula, $E = mc^2$. As a result of this reaction the surface of the sun is maintained at a temperature of approximately 5800 K. This energy is radiated away from the sun uniformly in all directions in close agreement with Planck's blackbody radiation formula. [4]

$$w_\lambda = \frac{2\pi hc^2\lambda^{-5}}{e^{\frac{hc}{\lambda kT}} - 1} \text{ (W/m}^2\text{/unit wavelength in meters),}$$

where $h = 6.63 \times 10^{-34}$ watt sec^2 (Planck's constant),
$K = 1.38 \times 10^{-23}$ joules/K (Boltzmann constant).

It propagates throughout the Solar System and the Universe mainly in the form of electromagnetic radiation of which light is only the visible part.

Solar radiation is mainly composed of:

- 48,0 % of visible light: $0,38 < \lambda \leq 0,78 \mu m$;

- 45,6 % infrared radiation (IR): 0,78 < ʎ ≤ 10µm;
- Ultraviolet (UV) radiation : 0,2 < ʎ ≤ 0,38µm.

The maximum illumination is between 450 nm and 700 nm.

In fact, the atmosphere absorbs mostly the IR and UV radiation and some of the visible light. Thus, the greater the thickness of the atmosphere crossed, the weaker the amount of energy received by the ground.

The light that comes to us from the Sun is white, that is to say, it is made up of all the colors of the rainbow, each with a different wavelength.

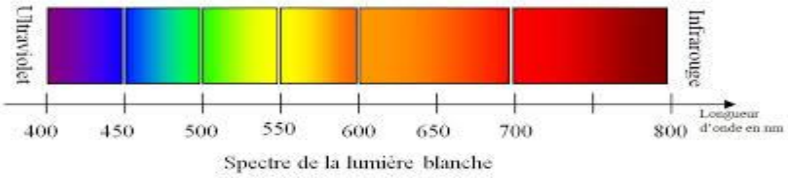

***Figure I-1**: white light Spectrum*

As the radiation passes through the atmosphere, it interacts with the gaseous constituents of the atmosphere (The air that makes up the earth's atmosphere consists of an incredible number of gaseous molecules (O2, N2, CO2, etc.), dust and tiny water droplets) and with all particles present in suspension (aerosols, water droplets and ice crystals), so it undergoes losses due to its partial absorption by gases and water vapor, as well as reflections from clouds and the ground.

On the other hand, this dispersion is not the same for all the wavelengths or, more simply, for the various colors of the rainbow. The dispersion is larger for the purple and blue (small wavelength) and smaller for the red (long wavelength). the blue is thus differed, but not the red, this is why the sky is blue during the day. In the morning and in the evening, the sunlight must pass through a thicker layer of the atmosphere, about 10 times larger than at noon. The diffusion of light of short wavelength (violet and blue) is so large that the light we perceive in the sky appears red to us.

II. 2. Variation of solar radiation as a function of the earth's movements

Detailed knowledge of the sun's position in the sky at any given moment from any point of view located on the earth makes it possible to understand and use the positioning of a solar collector (e.g. solar panel) for better conversion of solar radiation.

To locate a point M on the earth's surface, two angles are required [5] (**figure I-2**):

- **Latitude** φ : the astronomical latitude is the angle that the vertical of the place makes with the equatorial plane.
- **Longitude** λ **:** Longitude is the angle between the meridian of the place and the Greenwich .

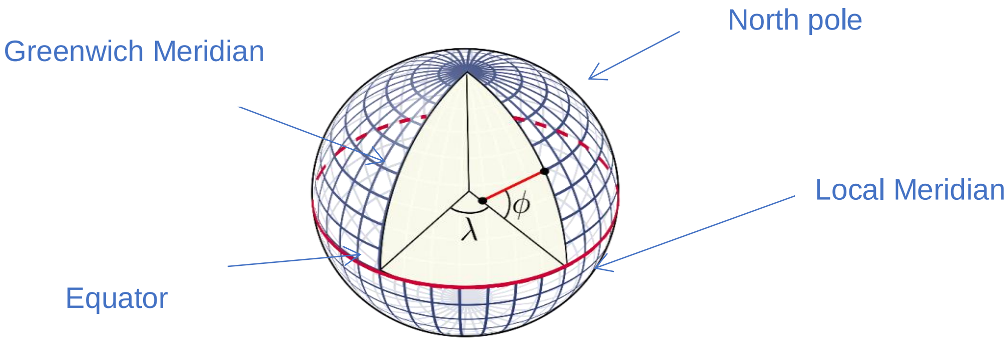

Figure I-2: Longitude and latitude of a point M on the earth's surface.

On the other hand, the earth's rotation on itself in one day in 24 hours explains the succession of days and nights and its revolution around the sun in one year (365 days) explains the succession of the seasons. But seen from the earth, the sun seems to move over half a sphere (**figure I-3**), the center of which is the observation point on earth, doing, during the day, a circular trajectory in the sky which is none other than the reflection of the real movements of the earth.

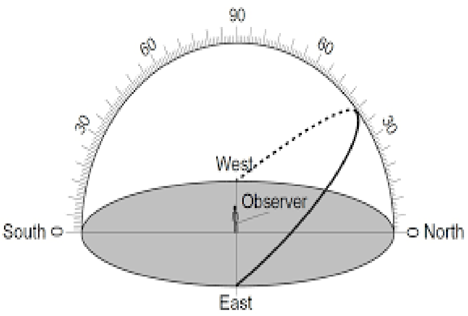

***Figure I-3**: Seen from the earth, the sun appears to follow a circular pa0th around an axis of apparent rotation passing approximately through the North Pole Star. Same thing happens to the stars by night. The only star that is motionless is the North Star.*

Over the course of the year, the (apparent) trajectory that the sun takes in the sky changes every day (**Figure I-4**) it rises more or less high in the sky; it rises and sets in different places and the day lasts more or less long, but all these trajectories are parallel to each other and perpendicular to the axis of the earth's apparent rotation. This axis of rotation is in the direction of the Pole Star: the only star standing still among all the revolving stars and pointing north.

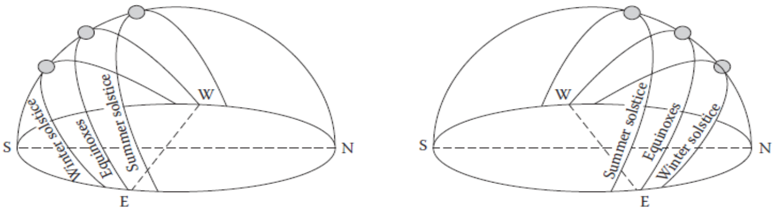

***Figure I-4**: Apparent daily path of the Sun in the sky throughout the year for an observer in the Northern (left) and Southern Hemispheres (right).*

The day of the **equinoxes** of spring and autumn, the sun describes the celestial equator. These are the only two days of the year when the sun rises exactly east and sets exactly west and where day and night are of equal length of twelve (12) hours. In this case, the area travelled by the sun is 180°.

On the day of the **summer solstice**, the sun reaches its highest point in the sky; it rises in the northeast and sets in the northwest and the sector travelled by the sun is 240°.

The day of the **winter solstice** is the time when the sun stays the longest down. It rises in the southeast and sets in the southwest with a covered area equal to 120°.

This change in the apparent trajectory (seen from the earth) of the sun during the year is due to the fact that the axis of rotation (the direction of which does not change) of the earth on itself is not perpendicular to the plane of the ecliptic (the plane of revolution of the earth containing the sun) but is inclined with respect to the ecliptic perpendicular by an angle equal to 23,43°(**Figure I-5**) [6]

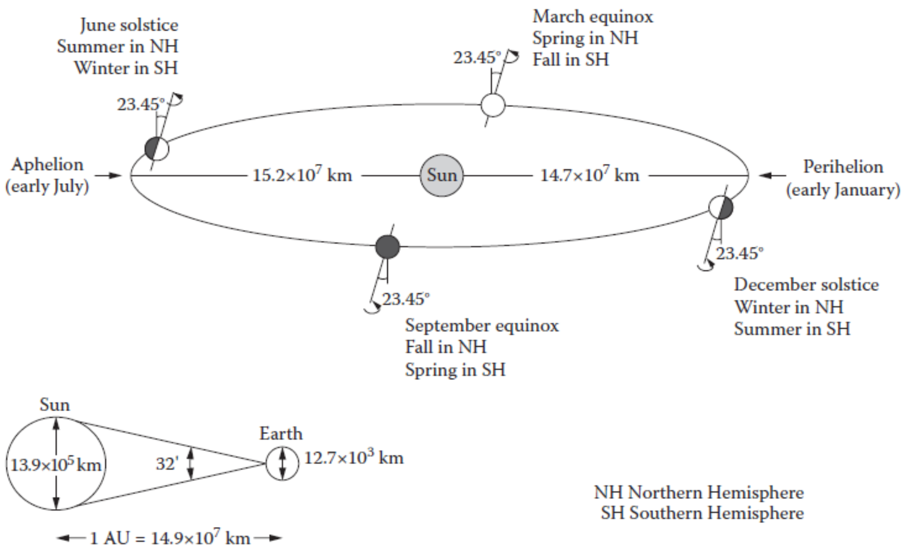

Figure I-5*: Four (04) remarkable positions of the earth in relation to the sun. The axis of rotation of the earth is inclined with respect to the vertical to the ecliptic plane at an angle 23, 43°. This results in declinations of the sun-earth direction.*

For this purpose, a graphical representation of the sun's path called the solar diagram is used, which is none other than an earthly view of the sun's movement. Thus, the position of the sun in the sky is referenced to an observer in the horizontal plane using two coordinates: height and azimuth,

The **height** of the sun is the angle between the direction of the sun and the earth (observer) with the horizontal plane.

The (geographic) **azimuth** is the angle of the projection of the direction of the sun-earth (observer) on the horizontal plane with the direction North-observer.

In order to plot the solar diagram, all the heights and azimuths of the sun during these daily trajectories over a year from the same observation point are taken. These measurements will be reported on a system of two axes: the heights on the vertical axis going from 0(for the horizon) towards 90(for the zenith) and azimuths on the horizontal axis. Therefore, the position of the sun at a given moment in the sky is represented by a point that is the intersection of two straight lines, one of which is the vertical representing the height of the sun and the other horizontal representing its azimuth. By locating the sun at different times of the day, we obtain the path of the sun.

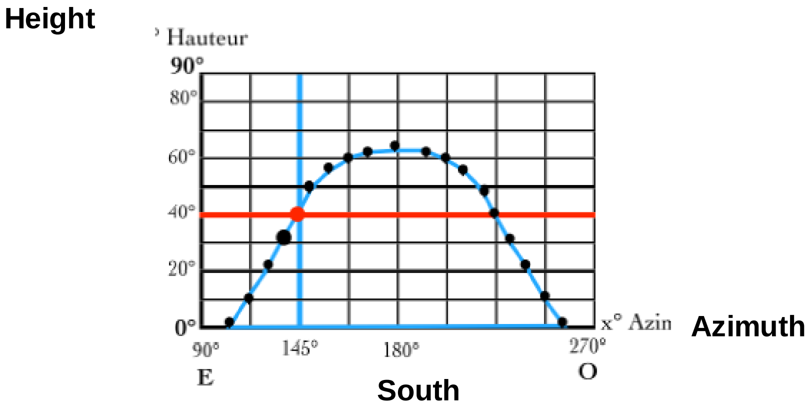

Figure I-6: On a solar diagram, the heights are plotted on the vertical axis and the azimuths are plotted on the axis horizontal. The position of the sun in the sky at a given moment is represented by a point on the plane

II. 3. Solar spectral distribution

The solar radiation that arrives on the ground is divided into three parts: a direct part that comes directly from the sun, a second part diffused by the atmosphere, and the other part reflected. The atmosphere and the earth also have their own radiation. The knowledge of these various radiations allows us to establish a radiation balance of the earth-atmosphere system.

- **Direct radiation** is received directly from the sun, without scattering by the atmosphere. Its rays are parallel to each other, so it forms shadows and can be concentrated by mirrors.
- **Scattered radiation** consists of photons scattered by fine particles or molecules of different sizes in the atmosphere (air, cloud cover, aerosols). That is to say, reflected in all directions.

- **The albedo** is the part reflected by the ground. Because in reality the earth is not a black body, it depends on the environment of the earth's surface, it will have to be taken into account to evaluate the radiation on inclined planes.

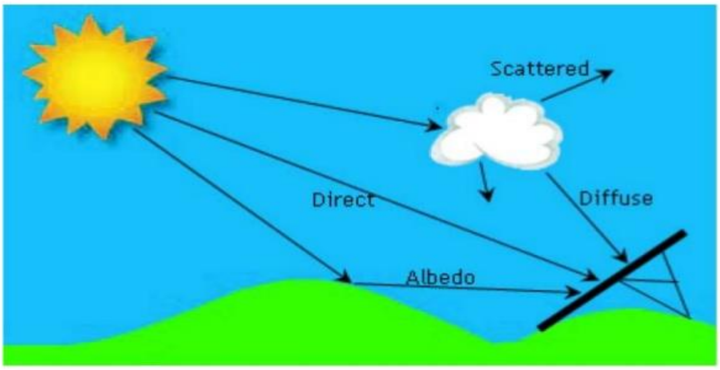

Figure I-7: *Components of solar radiation*

III. MEASURING SUNLIGHT

The electromagnetic radiation from the sun (including gamma rays, X-rays, Ultra-Violet, visible, Infra-Red, microwaves and radio waves) can be described in terms of electromagnetic wave characterized by a frequency ν and a wavelength λ, and also of photons, moving at speed of light (c= 3.108 m. s-1). The energy of this particle is given by the Planck-Einstein relation:

$$\mathbf{E= h\, \nu=}\frac{hC}{\lambda}$$

With the Planck's constant h= 6.6 x 10-34 J.s

However, not all of the electromagnetic radiation reaches the Earth's surface, the solar spectrum at Earth's surface is therefore dependent of many atmospheric parameters as seen previously as well as the path length through the atmosphere.

It is characterized by an Air-Mass coefficient, "AM X", and defined as the optical path length L through Earth's atmosphere, commonly used for terrestrial applications such photovoltaic solar cells.

When the Sun is directly at its zenith the Air-Mass indicator is denoted AM 1, "1" for one atmosphere with a solar irradiance at Earth's surface (at sea level more precisely) reaching 1040 W/m² in optimum conditions. This value is further reduced compared to the extraterrestrial solar radiation referred as air mass zero, AM 0, meaning no atmosphere.

For incident solar radiation at angle θ relative to the normal to the Earth's surface L0, the Air-Mass coefficient is expressed as:

$$AM\ X = \frac{L}{L_0} = \frac{1}{\cos\theta}$$

III. 1. The pyranometer

Since all the calculations and approximations in the world cannot yield exact predictions of the amount of sunlight that will fall on a given surface at a given angle at a given time at a given day in a given place, the design of photovoltaic power systems is dependent upon the use of data based on measurements averaged over a long time. The **pyranometer** is designed to measure global radiation. It is a heat flow sensor used to measure the amount of solar energy in natural light. The pyranometer is designed to respond to all wavelengths and, hence, it responds accurately to the total power in any incident spectrum. [4]

Many inexpensive instruments are also available for measuring light intensity, including instruments based on cadmium sulfide photocells and silicon photodiodes. These devices give good indications of relative intensity, but are not sensitive to the total solar spectrum and thus cannot be accurately calibrated to measure total energy. These devices also do not normally have lenses that capture incident radiation from all directions. [5]

Figure I-8*: Pyranometer for Measuring the irradiance of a Solar Farm, in a Solar Cell Factory*

III. 2. Surface property

When radiated photons or electromagnetic waves reach another surface, they may be absorbed, reflected, or transmitted. From an energy stand point, the sum of the absorbed, reflected, and transmitted fraction of radiation energy must be equal to unity:

$$\alpha+\rho+\tau=1$$

where

α is absorptivity (fraction of incident radiation that is absorbed)

ρ is reflectivity (fraction of incident radiation that is reflected)

τ is transmissivity (fraction of incident radiation that is transmitted)

III. 3. Black body radiation

Another key concept for solar energy is blackbody radiation. A blackbody is an ideal thermal radiator. It absorbs all incident radiation, regardless of wavelength and direction (absorptivity=1), it also emits maximum radiation energy in all directions (diffuse emitter). The emitted energy by a blackbody (blackbody emissive power, W/m2) is given by the Stefan–Boltzmann law (Incropera and DeWitt):

$$E=\sigma T^4$$

where σ is the Stefan–Boltzmann constant (σ= 5.67 × 10–8 W/m2K4) and T is the absolute temperature.

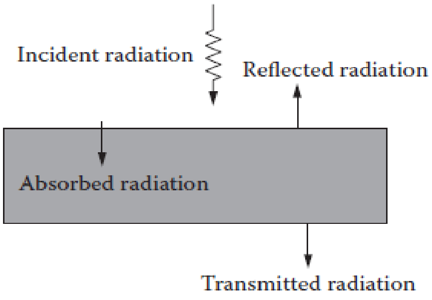

***Figure I-9**: Radiation surface properties*

IV. PHOTOVOLTAIC CELLS

IV. 1. Photovoltaic effect and the p-n junction

The photoelectric or photovoltaic effect discovered in 1839 by Antoine Becquerel and then highlighted by Heinrich Hertz in 1887 is defined as the process that allows the creation of moving electrons or holes (electron defects) in a material that absorbs the photons that illuminate it and constitutes the basic principle of photovoltaic cells [7]. Most inorganic PV cells are based on p-n junctions. The latter results from the combination of a p-type semiconductor (majority holes) and an n-type semiconductor (majority electrons). After contacting, the holes of the p semiconductor diffuse towards the n semiconductor and vice versa for the electrons of the n semiconductor. A zone free of free charge carriers then appears in the central area of the junction called the space charge zone (SZC). This is formed by fixed ions resulting from doping, and thus creates an internal electric field which opposes the diffusion of the majority carriers. After the junction is established, the photo carriers created in the neutral regions, which are free of electric field, generate diffusion currents, while those created in the Width Space Charge Zone, WZCE, are accelerated by the electric field towards the areas where they become majority carriers. Therefore, only the excess minority carriers are active in a p-n junction and participate in the generation of a current (sum of diffusion and drift currents).

IV. 2. Energy band gap

When light shines on a material, it is either reflected, transmitted, or absorbed. Absorption of light is the conversion of the energy contained in the light to another form of energy, typically heat. Some materials, however, happen to have just the right properties needed to convert the energy in the incident photons to electrical energy. When a photon is absorbed, it interacts with an atom in the absorbing material by giving off its energy to an electron in the material. This energy transfer is governed by the rules of conservation of momentum and conservation of energy. Since the zero-mass photon has very small momentum compared to the electrons and holes, the transfer of energy from a photon to a material occurs with inconsequential momentum transfer. Depending on the energy of the photon, an electron may be raised to a higher energy state within an atom or it may be liberated from the atom. Liberated electrons are then capable of moving through the crystal in accordance with whatever phenomena may be present that could cause the electron to move, such as temperature, diffusion or an electric field.

Semiconductor materials are characterized as being perfect insulators at absolute zero temperature, with charge carriers being made available for conduction as the temperature of the material is increased. This phenomenon can be explained on the basis of quantum theory, by noting that semiconductor materials have an energy band gap between the valence band and the conduction band. The valence band represents the allowable energies of valence electrons that are bound to host atoms. The conduction band represents the allowable energies of electrons that have received energy from some mechanism and are now no longer bound to specific host atoms. At T = 0 K, all allowable energy states in the valence band of a semiconductor are occupied by electrons, and no allowable energy states in the conduction band are occupied. Since the conduction process requires that charge carriers move from one state to another within an energy band, no conduction can take place when all states are occupied or when all states are empty. This is illustrated in Figure 10.a. As temperature of a semiconductor sample is increased, sufficient energy is imparted to a small fraction of the electrons in the valence band for them to move to the conduction band. In effect, these electrons are leaving covalent bonds in the semiconductor host material. When an electron leaves the valence band, an opening is left which may now be occupied by another electron, provided that the other electron moves to the opening. If this happens, of course, the electron that moves in the valence band to the opening, leaves behind an opening in the location from which it moved. If one engages in an elegant quantum mechanical explanation of this phenomenon, it must be concluded that the electron moving in the valence band must have either a negative effective mass along with its negative charge, or, alternatively, a positive effective mass and a positive charge. The latter has been the popular description, and, as a result, the electron motion in the valence band is called whole motion, where “hole” is the name chosen for the positive charges, since they relate to the moving holes that the electrons have left in the valence band. What is important to note about these conduction electrons and valence holes is that they have occurred in pairs. Hence, when an electron is moved from the valence band to the conduction band in a semiconductor by whatever means, it constitutes the creation of an electron-hole pair (EHP). Both charge carriers are then free to become part of the conduction process in the material. [8]

IV. 3. Doping

In order to change the electronic properties of a semiconductor material, we use Doping, which is the purposeful introduction of impurities into a semiconductor by controlling the number of electrons in the conduction band. Impurity atoms can be introduced into a material in two ways. They may be squeezed into the interstitial spaces between the atoms of the host crystal (called interstitial impurities) or they may substitute for an atom of the host crystal while maintaining the regular crystalline atomic structure (substitutional impurities). Note that a much smaller amount of energy is required to release an electron as compared to the energy needed to release one in a covalent bond. The energy level of this fifth electron corresponds to an isolated energy level lying in the forbidden gap region. This level can be called a donor level and the impurity atom responsible is called a donor. A concentration of donors can increase the conductivity so drastically that conduction due to impurities becomes the dominant conductance mechanism. In this case, the conductivity is due almost entirely to negative charge (electron) motion and the material is called an n-type semiconductor. Similarly, when a group impurity (boron) is introduced, there are only three valence electrons and the material have an affinity to attract electrons from the material, thus leaving a hole. Hole movements collectively create an energy level in the forbidden gap close to the valence band. This level can be called an acceptor level and the impurity atom responsible is called an acceptor. The material is called a p-type positive semiconductor with p-type impurities. [9]

V. PHYSICAL CHARACTERIZATION OF PHOTOVOLTAIC CELLS [10]

V. 1. Current/voltage characteristic and equivalent circuit

The **figure I-10** represents a current-voltage characteristic of a photovoltaic cell. According to the usual sign convention, the photocurrent in an ideal solar cell can be assimilated to a current source directed in the opposite direction of the diode characteristic in the dark, as shown in diagram c of **figure I-10**.

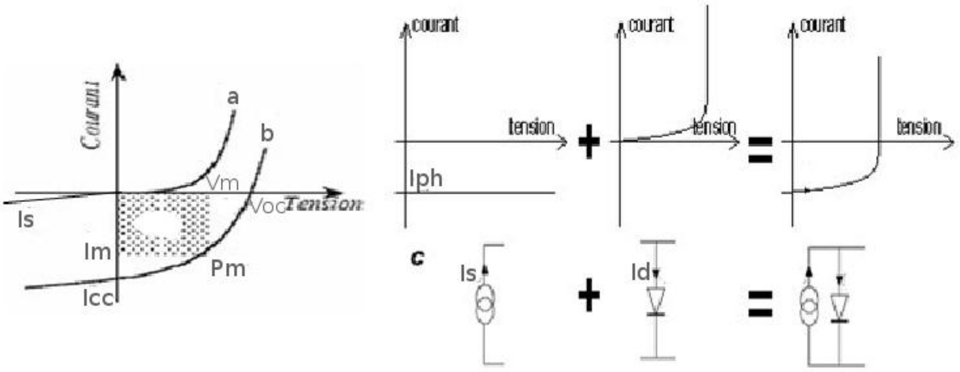

Figure I-10: Current/voltage characteristic of a PV cell: a) dark, b) under illumination, c) equivalent diagram of an ideal solar cell under illumination.

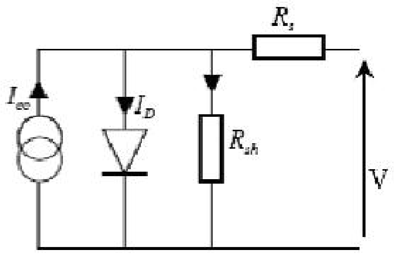

Figure I-11: Equivalent circuit of a solar cell

For an unlit solar cell polarized by a voltage V, the curve obeys the following Shockly equation:

$$I = \mathrm{Is}\left[exp\left(\frac{\mathrm{qV}}{\mathrm{nKT}}\right) - 1\right] \ (1.1)$$

where is the saturation current, q is the electron charge, k is the Boltzmann constant, T is the temperature and n is the ideality factor of the diode which takes into account recombination (in the ideal case it is equal to 1).

Under illumination, an additional inverse current Iph is added (taking into account the photocurrent)

$$I = \mathrm{Is}\left[exp\left(\frac{\mathrm{qV}}{\mathrm{nKT}}\right) - 1\right] - \mathrm{I}ph \ (1.2)$$

It is clear from **Figure I-10** that in total darkness, characteristic I (V) passes through the origin, whereas this is not the case in the presence of light radiation.

In the real case, contact resistances (resistivity of the electrodes and organic metal-material interfaces) and ohmic losses (due to the resistivity of the organic layers) as well as leakage currents (short-circuit currents) occur through the cell.

Figure I -11 shows the equivalent circuit of a real PV cell. R_s is a series resistance related to the volume resistivity and impedance of the electrodes and materials. It represents the inverse of the slope of the current-voltage curve at the point Vco. Rsh is a shunt resistor related to edge and volume recombination. It represents the inverse of the slope of the current-voltage curve at the point Icc. These resistors give in the real case an evaluation of the imperfections of the diode, and in general, the value of Rsh is greater than Rs (Rsh >>Rs). The ideal case is represented by: Rsh →∞ and Rs=0.

V. 2. Photovoltaic cell parameters [11]

The parameters of the photovoltaic cells (Icc, Vco, FF and η), extracted from the current-voltage characteristics, allow to compare different cells illuminated under identical conditions. These parameters are defined as follows:

I. 1. 1. *Short circuit current Icc*

The short-circuit current Icc is the current that flows through the junction under illumination without voltage application. It increases with the illumination intensity of the cell and depends on the illuminated surface, the wavelength of the radiation, the mobility of the carriers and the temperature.

I. 1. 2. *Open circuit voltage Vco*

The open circuit voltage Vco is the voltage measured when no current is flowing through the photovoltaic device. It depends mainly on the type of solar cell (pn junction, Schottky junction), the materials of the active layer and the nature of the active layer-electrode contacts. In addition, it depends on the illumination of the cell. we can easily get the expression of Vco in the case of a null current from the expression:

$$Vco = \frac{KT}{q}\ln(\frac{Iph}{Is}+1) \quad (1.3)$$

Two regimes can be observed depending on the degree of illumination (**Figure12**):

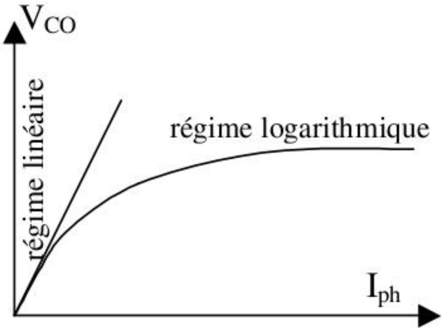

Figure I-12: Different speeds according to illumination power

I. 1. 3. *Fill Factor*

The power supplied to the external circuit by a photovoltaic cell under illumination depends on the load resistance. This power is maximum (noted Pmax) for an operating point Pm (Im* Vm) of the current-voltage curve (current between 0 and Icc and voltage between 0 and Vco).

The fill factor or form factor FF can be denoted by the following expression:

$$FF = \frac{Pmax}{VcoIcc} = \frac{ImVm}{VcoIcc} \quad (1.4)$$

I. 1. 4. *Efficiency η*

It represents the external energy efficiency of power conversion, values that affect the efficiency of solar cells are the band gap of the semiconductor, operating temperature, incident light, type and purity of the material, and parasitic resistances. It is defined by the following expression:

$$\eta = \frac{Pmax}{Pin} = \frac{FF\ Icc\ Vco}{Pin} \quad (1.5)$$

Pin represents the incident light power.

This efficiency can be optimized by increasing the form factor, short-circuit current and open circuit voltage. This is an essential parameter, as only knowing its value allows the performance of the cell to be evaluated.

VI. MAIN TYPES OF SOLAR CELLS

VI. 1. Inorganic photovoltaic cells

At present, the photovoltaic cells with the best photoconversion efficiency are based on the use of inorganic materials. Several types can be distinguished:

I. 1. 5. *Silicon-based cells*

Silicon is obtained from one or more crystals. Within this family, several types of cells using different qualities of silicon can be distinguished: mono-crystalline Si-based cells (efficiency of around 25%, high manufacturing cost), polycrystalline Si-based cells (efficiency of around 20%, lower manufacturing cost) and amorphous Si-based cells (lower efficiency and cost less than mono or polycrystalline).

I. 1. 6. *Monocrystalline silicon cells [12]*

Monocrystalline silicon cells offer the highest efficiency among commercially available solar panels: between 15 and 25%. These cells are made up of very pure crystals obtained by a strict and progressive control of the cooling of the silicon.

Figure I-13:*Monocrystalline silicon cell*

I. 1. 7. *Polycrystalline silicon cells (or multicrystalline)*

Modules using polycrystalline silicon cells generally have an efficiency of between 10 and 14%. These cells are simpler to manufacture and cheaper than monocrystalline silicon cells. Polycrystalline cells are recognizable by the irregular shapes of the crystals that are clearly visible to the human eye.

Figure I-14*: Monocrystalline silicon cell*

I. 1. 8. *Amorphous silicon cells*

Amorphous silicon cells are thin-film cells between 10 µm to 100-200 µm. They are manufactured by depositing a thin layer of silicon on a support (or "substrate"), (steel, glass, plastic ... etc.).

Figure I-15: *Amorphous silicon cells*

This technology reduces the manufacturing cost, but its efficiency is lower than that of crystalline silicon cells (around 5 to 8%), and is therefore reserved for applications requiring low power.

I. 1. 9. *Gallium arsenide-based cells*

A distinction must be made between two types of cells incorporating gallium arsenide. On the one hand, type III.V cells whose main component is gallium arsenide (yield of the order of 18 to 25%). On the other hand, multijunction cells (GInP/GaAs/Ge type) (efficiency of about 32%) but have a very high shaping cost.

I. 1. 10. *CIS or CIGS cells*

The former is composed of copper indium diselenide (CuInSe 2), while the latter also include gallium. This type of cell has a low manufacturing cost.

I. 1. 11. *Cadmium telluride (CdTe) cells*

The advantage of these cells lies in the high absorption of cadmium telluride; however, the toxicity of the material hinders the development of this technology. The yields obtained are of the order of 17%.

VI. 2. Organic photovoltaic cells

In the face of technology using inorganic materials, solar cells based on organic compounds are undergoing considerable development. Organic cells can be of several types:

I. 1. 12. *Schottky type cells*

This type of cell uses a p (or n) type semiconductor taken between two metal electrodes. The active area for photovoltaic conversion is between one of the metal electrodes and the semiconductor.

I. 1. 13. *Heterojunction cells of the bilayer type*

Two semiconductors, one p-type and the other n-type, are in contact forming a p-n junction. The active area is the interface between the two semiconductors.

I. 1. 14. *Interpenetrating network type heterojunction cells*

In this type of cell, p and n semiconductors are intimately mixed within a single layer. The contact area between the p and n semiconductors is multiplied by several orders of magnitude in comparison to bilayer cells, which increases the number of dissociated excitons

I. 1. 15. *Hybrid dye sensitized cells [12]*

Dye sensitized solar cells or Gratzel solar cells are photoelectrochemical cells. A basic type of electrochemical cell does not include a p-n or other junction between two solid inorganic semiconductors, but is composed of semiconductor electrode, an electrolyte layer and counter electrode, covered with Pt. The basis for both electrodes is the transparent TCO glass. TCO is short for transparent conductive oxides. Photoelectrochemical cell converts light to electric power with no net chemical change behind. At the interface between semiconductor and electrolyte, a space charge layer is formed, depending on the type of both semiconductor and electrolyte. In equilibrium, the chemical potential of electrons in the solid state is equal to the redox potential of the electrolyte Redox. Photons exceeding the band gap energy produce electron-hole pairs that are separated by electric field in the space charge layer. The electrons diffuse to the end of electrode and are transported through the external circuit with resistance. The holes are driven to the electrolyte interface, where they oxidize a molecule of redox pair. The oxidized molecule is reduced again by an electron that re-enters the cell through the external circuit.

VII. PHOTOVOLTAIC CONVERSION SYSTEM

A photovoltaic solar power plant is formed by a set of solar panels, connected to each other in series or parallel and connected to one or multiple inverters. These are used to transform the low-voltage DC current into high-voltage alternating current, directly usable by conventional devices.

However, the amount of energy obtained depends on a number of factors, namely, the surface area of the modules used, as well as their efficiency and the amount of sunlight that varies with latitude, season and weather.

A photovoltaic system is composed of several tools necessary to ensure an optimal electricity production. Any photovoltaic system can be composed, of three parts:

- One part of power generation.
- One part for the conversion of the energy generated.
- One part of energy storage.

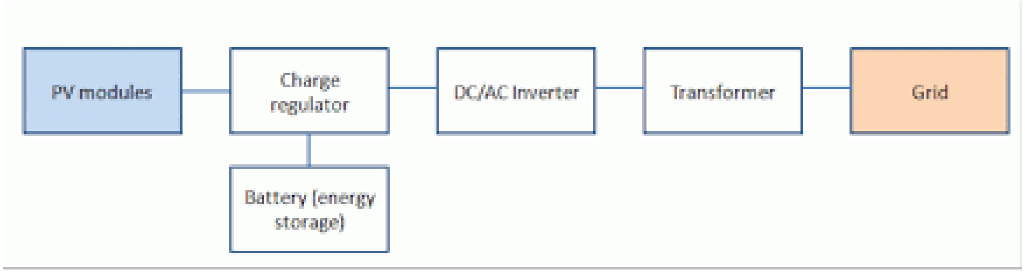

***Figure I-16**: Typical energy transformation path in a grid connected PV system*

These components depend on the type of the photovoltaic system. There are two types of systems:

VII. 1. STAND ALONE / OFF GRID

This type of installation is suitable for installations that cannot be connected to the network. Neither the building nor the panel are connected. The energy produced must be directly consumed and/or stored in accumulators to ensure that all requirements can be met.

These installations usually contain a **photovoltaic panel** to produce direct current, a **regulator** to protect the battery, an **inverter** that converts direct current into alternating current, and **batteries** that are charged during the day to provide power at night.

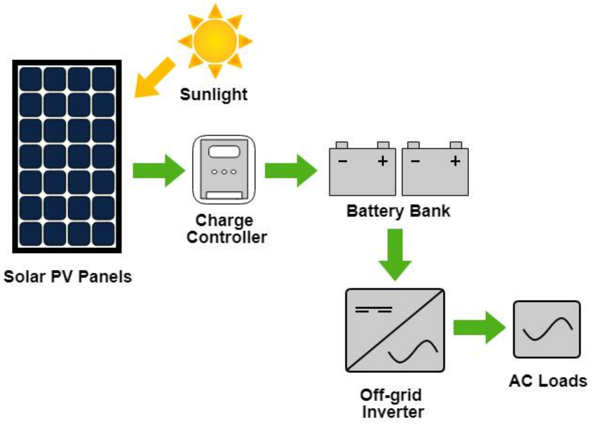

***Figure I-17**: example of an off grid photovoltaic system*

VII. 2. GRID CONNECTED

The photovoltaic system works as in isolated installations, but is connected directly to the public grid.

A grid-connected photovoltaic system consists of the following components:

- **Photovoltaic generator**: which should be exposed as much as possible in order to collect the maximum amount of sunlight over the year.
- **An inverter**: its role is to transform the direct current supplied by the photovoltaic generator into an alternating current having all the characteristics of the alternating current supplied by the electrical grid.
- **Safety and grid connection devices**: which ensure the protection of people and property.
- **A means of storing electricity**: possibly composed of batteries (lithium-ion, etc...).

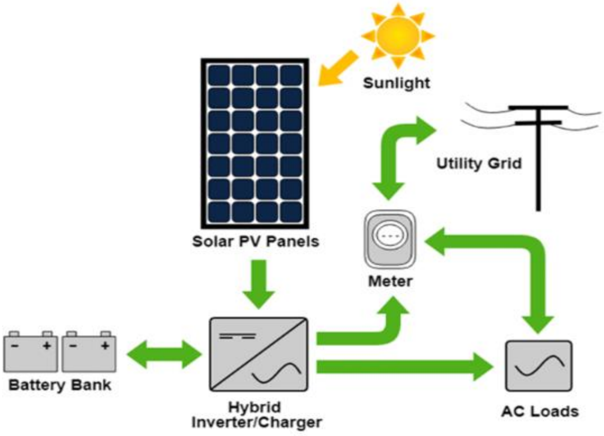

Figure I-18: *example of a grid connected system*

VII. 3. Power generation

Energy production is achieved by converting solar energy into electricity, this part is essentially composed of one or more modules. The photovoltaic panel consists of small cells that produce a very low electrical power (1 to 3 W) [13]. These cells are arranged in series to form a module or panel to produce higher power. The panels are finally interconnected with each other (in series and/or in parallel) to obtain a photovoltaic field.

VII. 4. Control system (regulation system)

In nearly all systems with battery storage, a charge controller is an essential component. The charge regulator has two main functions:

- Protection of the batteries against overcharging and deep discharge.
- Optimizing the energy transfer from the PV field to the application.

All photovoltaic systems must include careful regulation of battery charging and discharging, this is because the battery is one of the most fragile components of a PV system; its lifetime is closely related to the way it is charged and discharged.

The charge controller must shut down the load when the battery reaches a prescribed state of discharge and must shut down the PV array when the battery is fully charged (current reduction when the battery is almost fully charged, because when the current is too high a deformation of the electrodes inside can be caused, which could create a short circuit [13]**).**

When the “battery” is really a system of batteries connected in series and parallel as needed to meet system needs, the control process becomes somewhat of a challenge. The controller should be adjustable to ensure optimal battery system performance under various charging, discharging and temperature conditions.

There are several types of regulators:

VII. 4. 1. *Shunt regulator*

Suitable for small power applications with 1 or 2 PV modules. The shunt regulator controls the battery charge by safely short-circuiting the PV module. All shunt controllers require a non-return diode in series between the battery and the shunt element to prevent the battery from short-circuiting.

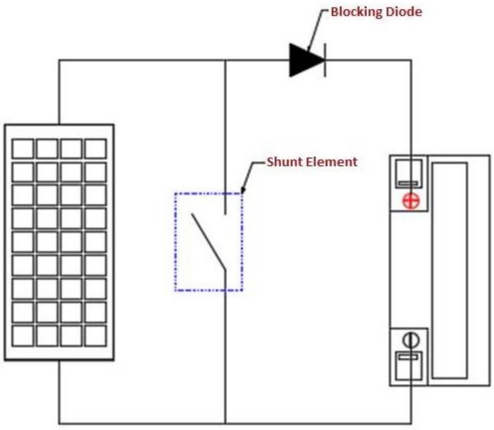

Figure I-19: *PV system including shunt charge regulator*

VII. 4. 2. *Serial Regulator*

Suitable for medium power applications with PV module currents above 10 A [13]. When the battery reaches full charge, the controller shuts off the current from the PV modules.

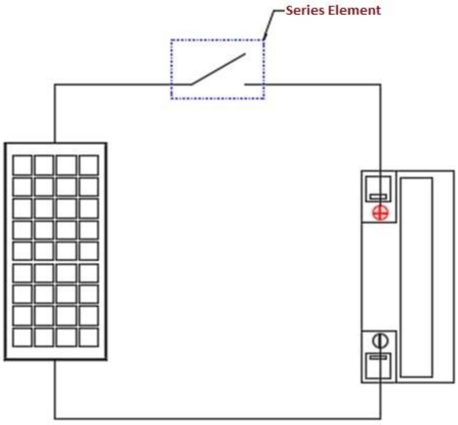

Figure I-20*: PV system including series charge regulator*

VII. 4. 3. *MPPT controller*

Suitable for high power applications. Ensures maximum power recovery from PV modules by continuously measuring current and voltage.

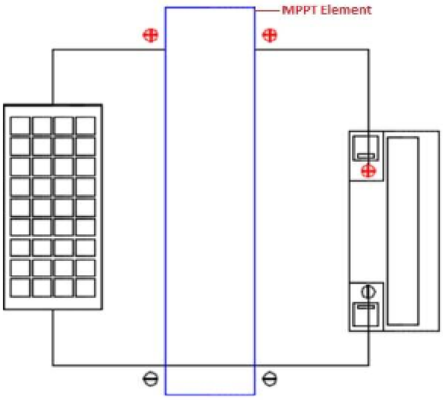

Figure I-21: *PV system including MPPT controller*

VII. 5. Converter system

The energy conversion system is usually located either between the PV field and the load (without storage with DC charging, DC-DC converter) or between the battery and the load (in this case it will be called inverter or DC-AC converter).

VII. 5. 1. *The DC-DC converter*

This type of converter is designed to adapt at any time the apparent impedance of the load to the impedance of the PV field corresponding to the point of maximum power. This matching system is commonly called MPPT (maximum power point tracking). Its efficiency is between 90 and 95% [13].

VII. 5. 2. *The DC-AC converter*

In order to supply devices that operate on alternating current, a converter must be interposed between the battery and these devices. The most commonly used converters convert the direct current from the battery into 220 V/50 Hz or 380 V/50 Hz alternating current. [13]

VII. 5. 3. *Energy storage*

In intermittent power generation systems, particularly photovoltaic systems, it is essential to be able to store energy in order to adjust production to consumption. This is particularly true for systems which are not connected to a power grid, even when the electrical grid is present, the use of storage makes it possible to smooth intermittent production and inject energy during the most relevant periods (night and "sunless" days).

The storage system is a crucial part of the photovoltaic installation from a technical point of view, but also from an economic point of view, as it accounts for 40-50% [13] of the cost of the installation.

VIII. ECONOMICS

VIII. 1. Solar energy is free, but what does it cost?

Solar energy is free, but this doesn't make it cheap. Over the past few decades, solar products had known a remarkable cost reduction, thus, small- and medium-scale uses home applications are still relatively expensive [14]. Having a home designed to use solar power won't cost more than a regular home, even much less operating costs. The basic difference between them is that the solar-energy house is fed by the sun, it needs smaller systems that cool/ heat it, while poorly designed homes fight the Sun and are very cold in winter and extremely hot in summer [15]. Industrial and modern agriculture societies were founded on fossil fuels (coal, oil, and gas). As energy demand increases due to developing countries modernization, increased fuel prices will force alternatives to be introduced. The world will make a gradual shift throughout the twenty-first century technologies that harness clean energy sources such as sun and wind [14]. As the full effect and impact of environmental externalities such as global warming become apparent, society will demand cleaner energy technologies and policies that favor development of a clean-energy industrial base. The cost of technologically driven approaches for clean energy will continue to fall and become more competitive. Eventually, clean energy technologies will be the inexpensive solution. By the end of the twenty-first century, clean-energy sources will dominate. This will not be an easy or cheap transition for society, but it is necessary. Already, solar energy is cost effective for many urban and rural applications. Solar hot-water systems are very competitive, with typical paybacks from 5–7 years as compared to electric hot water heaters (depending on the local solar resource). For sites that are remote from the electric grid, PV systems are already cost competitive, although they are also popular for on-grid applications as environmental “elitists” try to demonstrate that they are “green.” However, installing grid-tied PV systems without making efforts to install energy-efficient equipment first for people and companies working in the field of “green-washing” should be aware of their efficiency. The solar energy usage is not only for reducing carbon emissions, far more can be achieved through that energy conservation. The decision to use a solar energy system over conventional technologies depends on the energy security, economic, and environmental benefits expected. It is fact that the investment cost in Solar energy systems; but in the other hand, they do not require fuel and often require little maintenance. The traditional business entities have always couched their concerns in terms of economics, judging that a clean environment is uneconomical or that renewable energy is too expensive. Due to the lack of maintenance and long-term life cycle costs of a solar energy system should be understood to determine whether such a system is economically viable. [16]

VIII. 1. 1. *Cost of Energy [17]*

The cost of energy (COE) is primarily driven by the installed cost and the annual energy production. For PV systems, that cost is determined primarily by the cost of the modules. For on-grid systems, PV costs are from ab out \$6–\$8/Wp. After losses, each Watt produces 2–6 Wh/day, depending on solar resource; this translates to about \$0.22–\$0.35/kWh. The cost of remote stand-alone PV systems with batteries will be from 1.5–2 times more than grid-connected systems. High-quality industrial batteries last 7–9 years; others last 3–5 years.

VIII. 1. 2. *PV cost [18]*

For many applications, especially remote-site and small-power applications, PV power is the most cost-effective oAn LCCption available. Generating clean electric power on site without using fossil fuel is an added benefit. Capital costs are high for PV, but fuel costs are nonexistent. PV module costs have dropped by an order of magnitude over the past two decades. New PV modules generally cost about \$3 per Watt, depending on quantities purchased. Off-grid PV systems with battery storage typically run from about \$12 to \$15 per peak Watt installed, depending on system size and location. Grid-tie PV systems are averaging \$6–\$8 per Watt installed, also depending on system size and location.

Larger PV water pumping systems with all balance-of-system components, including the pump, can be installed for under \$10 per Watt. A well-designed PV system requires minimal maintenance, which leads to significant labor and travel savings. PV modules on the market today are guaranteed for about 25 years and quality crystalline PV modules should last over 50 years. It is important when designing PV systems to be realistic and flexible and not to overdesign the system or overestimate energy requirements. PV conversion efficiencies and manufacturing processes will continue to improve, causing prices gradually to decrease. It takes many years to bring PV cells from the laboratory into commercial production, so overnight breakthroughs in the marketplace should not be expected.

VIII. 1. 3. *Life cycle cost [19]*

In order to gain a true perspective of the economic value of solar energy systems, it is necessary to compare solar technologies to conventional energy technologies on a life cycle cost (LCC) basis. This method permits the calculation of total system cost during a determined period of time, considering not only initial investment but also costs incurred during the functioning time of the system. The LCC is the “present value” life cycle cost of the initial investment cost, as well as long-term costs directly related to repair, operation, maintenance, transportation to the site, and fuel used to run the system. Present value is understood as the calculation of expenses that will be realized in the future but applied in the present. An LCC analysis can determine the total cost of the whole system, including all expenses incurred over the functioning time of the system. The main reasons to do this LCC analysis are comparing different options of power technology, and determining which one has the most cost-effective system designs. For some renewable energy applications, there are not any options to small renewable energy systems because they produce power where there is no power. For these applications, the first estimated cost of the system, the infrastructure needed to start using the system and maintaining its good performances, and the price people pay for the energy are the main concerns. A LCC analysis permit studying the effect of using different components with different reliabilities and lifetimes. For instance, a less expensive battery might be expected to last 4 years, while a more expensive battery might last 7 years. Which battery is the best to buy? This type of question can be answered with an LCC analysis:

$$\mathbf{LCC=C+Mpw+Epw+Rpw-Spw}$$

where

LCC = life cycle cost.

C = initial cost of installation mince (-) the actual value of the coast equipment, including system design, engineering, and installation additional cost).

Mpw = sum of all operation and maintenance yearly costs mince (-) the present value of expenses due to operation and maintenance programs.

Epw = the coast of energy, sum of fuel costs of all years mince (-) the cost of fuel consumed by the conventional pumping equipment.

Rpw = sum of replacement costs of all years mince (-) the actual cost of replacement components anticipated over the operating time of the system.

Spw = salvage value mince (-) net worth at end of final year.

Future costs must be discounted because of the changes that may occur on the money's value over time, so the present worth is calculated for costs for each year. Life span for PV is assumed to be 20–25 years. Life cycle costing is the best way of purchasing decisions. On this basis, many renewable energy systems are economical. The financial evaluation can be done on a yearly basis to obtain cash flow, breakeven point, and payback time.

IX. PHOTOVOLTAIC APPLICATIONS

Solar cell technologies are used for two main applications, namely space and terrestrial applications. The PV solar systems are already an important part of our lives. The simplest PV solar systems power are in many of the small calculators and wrist watches that we use every day. More complicated systems provide electricity for pumping water, powering communications equipment, and even lighting our homes and running our household appliances. At present, there are four primary market areas for photovoltaic terrestrial applications:

- Consumer products, such as watches, calculators, and lanterns.
- Off-grid, power systems, such as solar home systems for individual households.
- Off-grid industrial power systems for water management, lighting, and telecommunication.
- Grid connected PV systems that are integrated in roofs and outer walls of buildings or in noise barriers along the motorways.

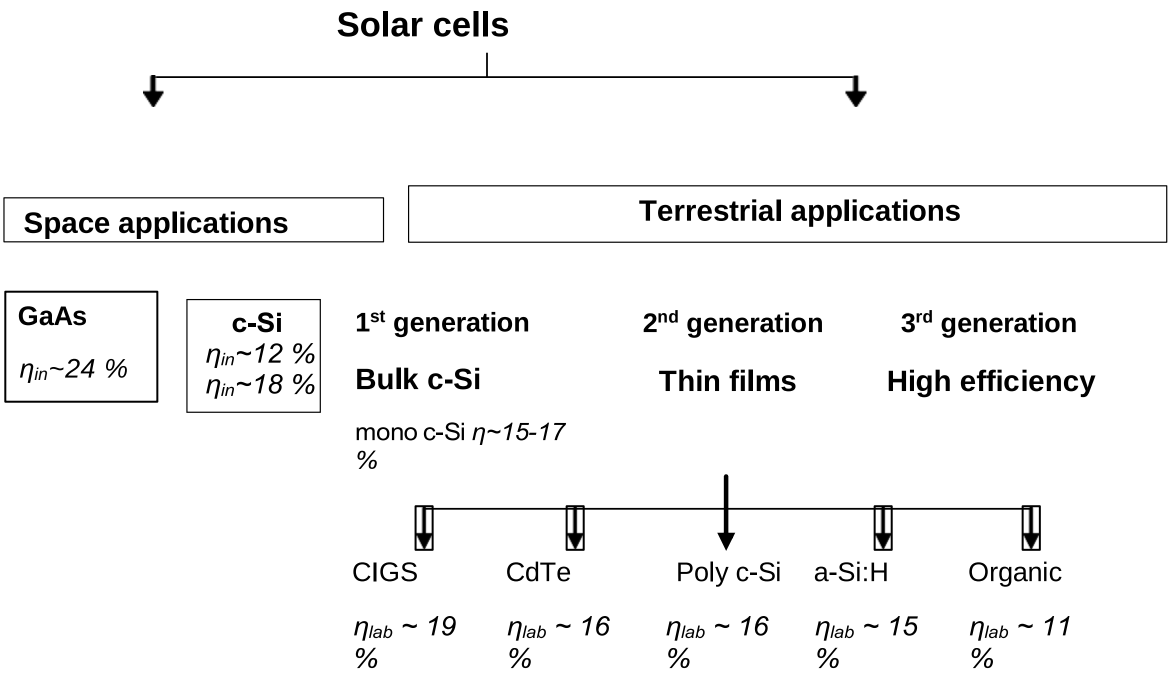

***Figure I-22**: Overview of solar cell applications and of several types of solar cells used in different applications.*

X. ENVIRONMENTAL IMPACT

Electrical energy is the axis of all growth efforts in both the developed and the developing nations because conventional energy sources are finite and fast depleting. In the last decades, energy related problems are turning into major issues and involve the ideal use of resources, the environmental impact due to the emission of pollutants and the consumption of conventional energy resources.

Using solar energy can have a positive effect on the environment when solar energy replaces the use of other energies that have larger effects on the environment. Solar energy systems do not produce air pollution, water pollution, or greenhouse gases. PV modules generate electricity directly from light without emissions, noise, or vibration. But large solar power plants can affect the environment.

Solar energy has low energy density: PV modules require a **large surface area** for small amounts of energy generation. Near their locations, clearing land for construction and the placement of the power plant may have long-term effects on the habitats.

Some solar power plants may require **water** for cleaning solar collectors and concentrators or for cooling turbine generators. Using large volumes of ground water or surface water may affect the ecosystems that depend on these water resources.

In addition, the beam of concentrated sunlight a solar power tower creates can kill birds and insects that fly into the beam.

Furthermore, some **toxic materials** and chemicals are used to make the photovoltaic (PV) cells that convert sunlight into electricity. Some solar thermal systems use hazardous fluids to transfer heat. Leaks of these could harm the environment. During the life of the PV system, substances are not emitted that might be harmful to the health or environment. However, a great amount of energy is needed in their production.

And of course, at the **end of their useful life**, the installation must be disposed of and the residues dealt with.

X. 1. Environmental Effects of PV System Production

X. 1. 1. *Hazardous materials*

The production phase of each PV technology can be described in terms of a production cycle, which includes potential pollutants or hazardous waste associated with each production step. Perhaps the most important common denominator associated with all PV technologies is the material used for cleaning the cells. The PV cell manufacturing process includes hazardous materials, most of which are used for the cleaning and purifying of the semiconductor surface. In all cases, high levels of cleanliness are required to maximize performance, and in some cases the solvents used are highly toxic. The common means of dealing with these solvents is to confine them and then recycle them.

X. 1. 2. *Life cycle and global warming emissions*

While there are no global warming emissions associated with generating electricity from solar energy, there are emissions associated with other stages of the solar life-cycle, including manufacturing, materials transportation, installation, maintenance, decommissioning and dismantlement. Most estimates of life-cycle emissions for photovoltaic systems are between 0.07 and 0.18 pounds of carbon dioxide equivalent per kilowatt-hour.

X. 1. 3. *Recycling*

What happens when solar panels are no more of use?

Although solar panel recycling has not become a major problem yet, it will in the coming decades because solar panels need to be replaced. When solar panels break, it is possible that they leak chemicals which are sealed in a functional module. If solar panels are not disposed of properly, chemical leaking may be a widespread issue. [20]

X. 2. Environmental Effects of PV System Deployment and Operation

X. 2. 1. *Land use*

Depending on their location, larger utility-scale solar facilities can raise concerns about land degradation and habitat loss. Total land area necessities differ depending on: technology, topography of the site, and the intensity of the solar irradiance.

Impacts on land from utility-scale solar systems can be minimized by placing them at lower-quality locations like brownfields, abandoned mining land... Smaller scale solar PV arrays, which can be built on homes or commercial buildings, also have minimal land use impact.

X. 2. 2. *Deployment*

The deployment of PV systems has associated environmental and health costs similar to the deployment of other energy technologies. Steel, aluminum and concrete can be expected to be part of the structures upon which the PV arrays and associated components will be mounted.

X. 2. 3. *Water use*

Solar PV cells do not use water to produce electricity. However, some water is used to manufacture solar PV components.

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Chapter II : DYE SENSITIZED SOLAR CELLS

I. INTRODUCTION

Since the creation of the first photovoltaic panel by three American researchers (Pearson, Prince and Chapin) in 1954 for a space application, solar technology has continued to progress. Apart from the widely used silicon-based panels, other technologies have shown great potential and conversion efficiencies well above the 6% obtained by these three American researchers. Since 1976, the National Renewable Energy Laboratory (NREL) has maintained a record-breaking table of research-based solar cell efficiencies. Typically, these technologies are classified into two categories, which will be described in the following sections:

- Solar technologies based on inorganic materials

- Solar technologies based on organic materials

The conversion of solar energy into electrical energy in photovoltaic cells is based on the photovoltaic effect. In short, it consists of the generation of electric charges as a result of an excitation of the material caused by the absorption of photons. The charges then diffuse from the material to an external electrical circuit via electrodes. These generation and transport processes involve the use of semiconductor-type materials as the basic element of photovoltaic cells.

Nowadays, photovoltaics represents an important state in renewables and more generally in energy. Indeed, a panel is a clean technology that has a largely positive carbon balance on its own energy consumption. It blends into the landscape without any nuisance or impact on the ecosystem and reduces losses related to the transport of energy. The first panels were made of selenium, then they were replaced by panels made of silicon. There are several types of solar panels: Panels composed of monocrystalline silicon cells, Panels made of polycrystalline silicon cells, Amorphous thin-film silicon cell panels. However, the real challenge of photovoltaics is to reduce the amount of energy used to produce electricity and the cost per kilowatt-hour produced. Silicon currently is the best but its purification and treatment leads to very high costs to a manufacturing process that is highly toxic to the environment and very expensive. All of this...is a major obstacle to the development of photovoltaics. This is why alternative solutions are being developed using semiconductor materials other than silicon: titanium oxide, chalcogenides, and not requiring the use of rare materials.

A more original solution is to draw inspiration from nature (biomimicry) in the case of plant photosynthesis t. Dye photovoltaic cells are developed with this in mind. Photosynthesis is an endothermic process that occurs in the plants and in a certain organization and thanks to it unicellular energy, solar energy is transformed into chemical energy, which is included in glucose molecules, and in the bond of other organic substances. Now we found the connection between the cell and the process of photosynthesis: both of them convert solar energy, the first in electrical energy, the second in solar energy.

Because of the above-mentioned link Michael Grätzel, Professor of the physics of chemistry at the University of Lausanne in Switzerland, in 1991 showed the photovoltaic cell based on the process inspired by the photosynthesis of plants. The Grätzel cell, Through the successful recombination of nanostructured electrodes and injection of dye-stuff charges, Professor Grätzel and his colleagues have developed a solar cell with an energy conversion efficiency of more than 7% in 1991 and 10% in 1993. This solar cell is called Dye-Sensitized Solar Cell.

The ability to significantly modify the chemical and physical properties of organic compounds by a fine tuning of their structures constitutes the principal reason for expanding research and increased industrial interest in organic photovoltaics. In the future, they could represent a reliable solution at low cost and with a high return.

In this chapter, organic photovoltaic technology is introduced from a brief description to the principle of operation. After that, we will see a more detailed overview on the DSSC.

II. HISTORY [1]

The discovery of the photovoltaic effect is commonly attributed to the physicist **Becquerel**, who observed a photo-current when platinum electrodes, covered with silver bromide or of silver chloride, are illuminated in an aqueous solution.

In **1873** and **1876**, **Smith and Adams** filed the first reports on photoconductivity, respectively. The Commission has also decided to take a further step forward by working on selenium.

Anthracene was the first organic component where photoconductivity was observed by **Pochettino** in **1906** and **Volmer** in **1913**, and in the late **1950s** the potential use of organic materials as photoreceptors for imaging systems has been recognized.

In **1954**, the first inorganic solar cell was developed at Bell Laboratories. It was based on the Si and had a yield of 6%, so the scientific interest and commercial potential has led to increased research in photoconductivity.

In **1986**, **Tang** published the first organic heterojunction, followed 5 years later by **Hiramoto** who designed the first interpenetrating structure based on small molecules by co-evaporation.

Three years later, the first heterojunction in the polymer=C60 volume was attributed to Yu. The latter fabricated with the collaboration of **Hall** the first heterojunction polymer=polymer in **1995**.

In **2001**, **Schmidt-Mende** produced a self-assembled solar cell based on liquid crystals of hexabenzocoronene and perylene, and a few years later, in **2008**, the company Fujikura (manufacturer of electronic compounds), has succeeded in operating an organic photovoltaic cell of the DSSC (Dye-Sensitized Solar Cell or Gratzel cell) continuously at a temperature of 85°C and a humidity level of 85%, for 1,000 hours.

With improved conversion efficiency and reduced production costs, the photovoltaic market is now developing considerably in recent years, and the substitution of the photovoltaic of silicon by organic materials is considered a promising alternative for various reasons: low cost, unlimited raw material, ease of implementation, technology of low temperature, large surfaces, flexible devices...

III. BIOMIMICRY

Nature magazine expresses that: “basic research on the character of the natural mechanisms, from the elephant to the protein, enrich the panel from which creators and engineers draw their ideas. The possibilities to expand this panel are immense” **[7].** The creations designed by the Nature are an extraordinary resource, the scientific community has just realized that we must use these examples in our lives on a daily basis. Also, the proper use of this resource will certainly lead to a rapid development of technological processes. The expert in biomimicry Janine M. Benyus said that mimicking nature will allow us to make progress in several domains, she cites as examples the mechanisms inspired by leaves that run on solar energy.

Nature's creations guarantee the best productivity with less effort and using a minimum of material. They are capable of repair, are compatible with their environment and are fully recyclable. They are quiet, pleasant looking and easy to clean. And are a source of longevity. All these qualities are present in the models to imitate. The High-Country News says: "By using the natural systems as models, we can create technologies that are much more powerful and durable than those used today." **[8]**

III. 1. What is biomimicry?

Biomimicry is an innovative method that seeks sustainable solutions based on concepts and strategies that have proven their worth in nature, such as the solar collector that imitates plant leaves. The goal is to create new products, processes and protocols better suited for extended life on earth. Around the world, the followers of this method are learning a lot, their models are organizations that work without using the manufacturing principle of "heat-pressure treatment", of the ecosystems that are powered by solar energy and interactions, that create opportunities rather than waste.

Not only can biomimicry help the human species prolong its passage on the planet, but it can change the way we evaluate the nature around us. It can change the way we see and understand the world. In the role of the student who, rather than studying an organism, prefers to learn from it, we deepen our respect for nature. Respect leads to gratitude, and from gratitude comes a burning desire to protect the nature around us. **[9]**

III. 2. Nature runs on solar energy

At a time when we are faced with the gradual extinction of fossil fuels and the share of renewable energies our consumption is constantly increasing, often more out of necessity than choice, living organisms have always captured and used the sun as a stable and sustainable source of energy, while the system we have chosen will soon have spent all the energy it needs. Inspired by this observation, scientists have, studied the structure of a leaf in order to invent more efficient photovoltaic cells, from a biomimetic perspective that has proved to be successful. Indeed, the possibility of using sunlight on a large scale as a major source of primary energy could become a reality in this century. At the Unlike conventional silicon-based cells, the principle of the functioning of the dye cells is based on the natural process of the photosynthesis; i.e. the processes of light absorption and the load separation is differentiated and carried out by different materials. Each molecular component performs only one function, for which it is optimized. Another interest of these cells lies in their low cost because they are based on cheap materials and inexpensive technology. The principles governing the functioning of Photovoltaic cells based on the sensitization of a wide-band gap mineral oxide semiconductor called "Grätzel type" will be presented.

IV. COMPARISON BETWEEN THE ORGANIC AND INORGANIC TECHNOLOGIES:

the payback time (In order to compare the different renewable energy technologies, it is possible to calculate the energy payback time of these panels or EPBT, the time required for the module to produce the same amount of energy as it took to manufacture it), of first and second generation solar cells is about 2 years (except CdTe). However, it can be seen that the technologies based on organic materials can achieve payback times of less than 1 year, close to other green energies (about 6 months). This clearly shows the competitiveness of these new technologies compared to the older ones.

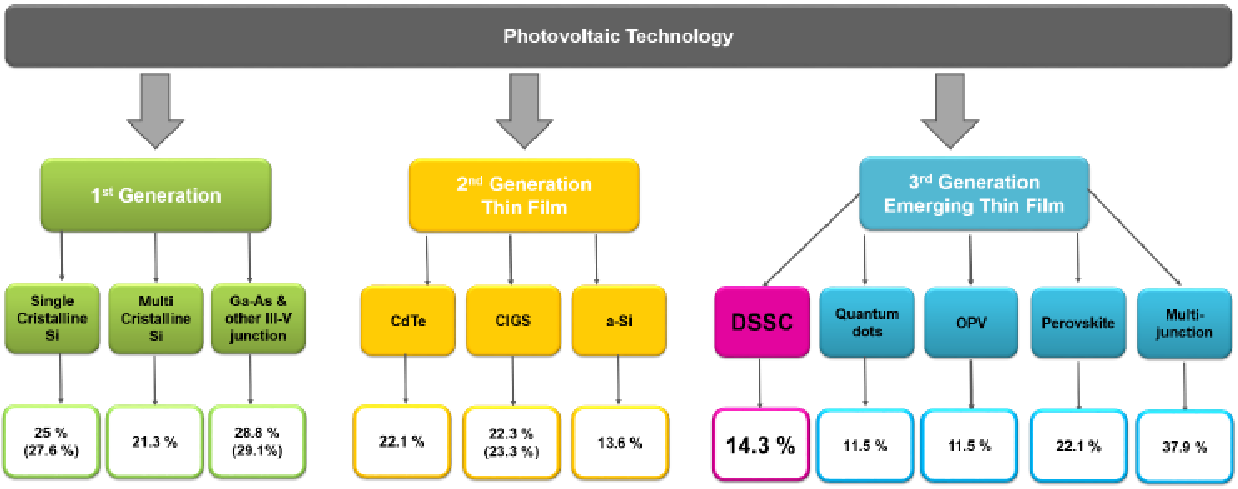


***Figure II-1**: comparison between the yields of photovoltaic technologies*

In terms of energy production, the different photovoltaic technologies all have different conversion efficiencies measured under standard conditions, but this does not account for the power output of each of these modules over a given period of time.

In 2011, Dyesol measured the energy accumulated over the course of a day (**Figure02**) with DSSC, Silicon, CIGS and CdTe modules. On a sunny day, the Silicon, CIGS and CdTe modules produce approximately the same amount of energy (~4 Wh) while the DSSC module produces more with a total of 6 Wh. This is even more true on a cloudy day (1.2 Wh in DSSC compared to <0.8 Wh for other technologies) **[2].**

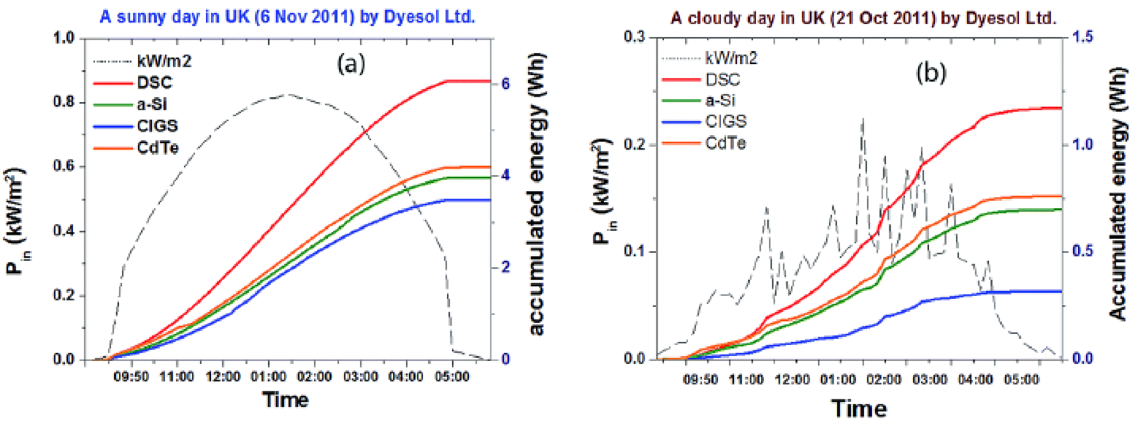


***Figure II-2**: Graphs representing the accumulation of energy produced over the period of a day with sunny and cloudy weather.*

Indeed, DSSC panels will be effective during periods of diffused light (morning and evening) as opposed to inorganic panels whose yields drop drastically when the light intensity decreases. Dye solar cells have many advantages, but there are still many technological challenges to be met. This manuscript will focus more particularly on this technology of dye-sensitized cells whose operation will be detailed in the following sections.

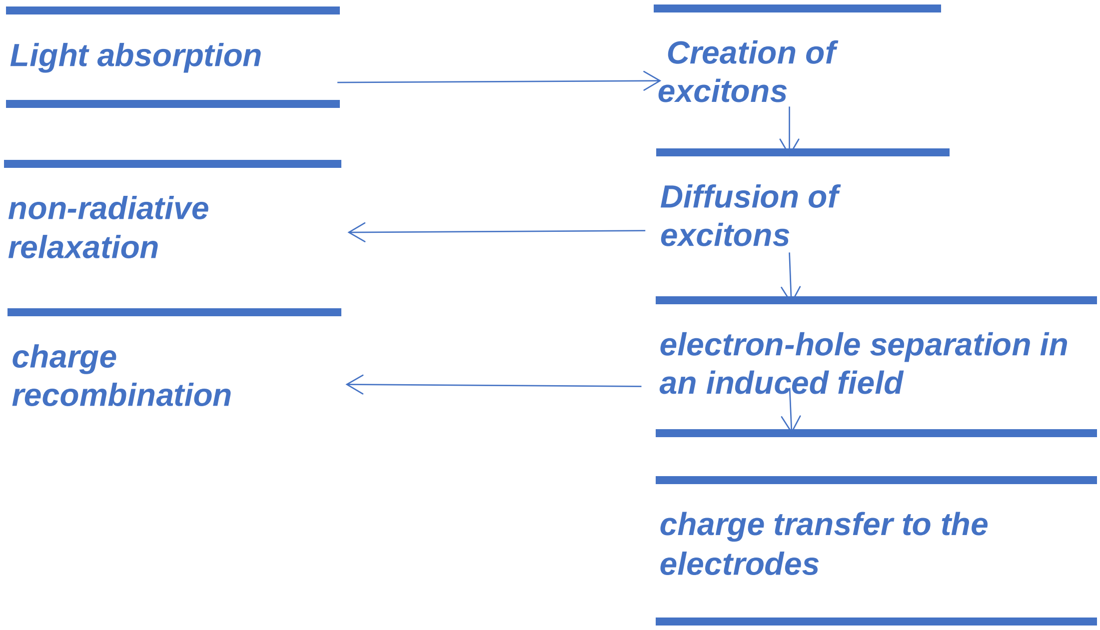
V. ORGANIC SEMICONDUCTOR

The semiconductor character of an organic material is due to the presence of a conjugated system, i.e. alternating single and double bonds. The difference in the length of the bonds makes it possible to envision two energetically equivalent resonant forms. In single-electron theories where the interactions between electrons are neglected, the existence of these two forms in one-dimensional materials can be explained in terms of Peierls distortion. The gain in electrical energy due to the stabilization of energy levels is greater than the elastic energy required to deform the polymer chain. The distortion results in the opening of a band gap between the energy levels, for an energy equal to the Fermi EF level.

This terminology is borrowed from the physics of inorganic semiconductors. It should be noted that it is not directly transposable to organic semiconductors. The absence of a three-dimensional crystal lattice, energy differences between intra- and intermolecular interactions, local structural disorder and chemical impurities make it more difficult for the model to describe the energy bands. **[10]** It should therefore be kept in mind that the classical strip model is an approximation in the case of organic semiconductors, but that it allows to apprehend qualitatively most of the phenomena observed in these materials.

VI. PHOTOVOLTAIC EFFECT IN ORGANIC CELLS:

After a general overview of how a photovoltaic solar cell works in chapter1, we will look at all the processes involved in the conversion of light into electrical energy within organic cells. the conversion of light into electrical energy involves a set of physical processes:



VI. 1. Incident photon absorption and exciton generation:

The absorption of light in photoactive organic layers results in the creation of a mobile neutral excited state called exciton, which is actually an electron-hole pair very closely linked-by compared to that produced in inorganic solar cells.

Basically, there are two types of excitons: Frenkel exciton (small, strongly bounded) and Wannier exciton (weakly bounded, large electron-hole distance). **Figure I-3**

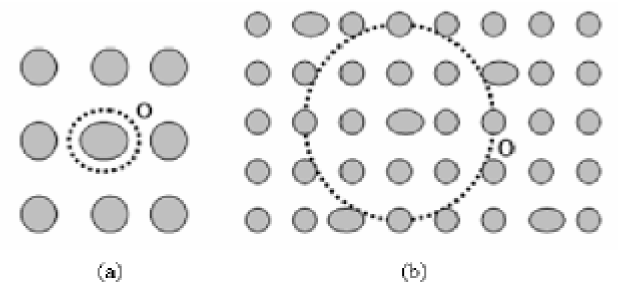


Figure II-3: representation of the Frenkel exciton (a), representation of the Wannier exciton (b)

VI. 2. Diffusion and dissociation of excitons

The movement of the exciton in the material is carried out by jumping from one molecule or polymer chain to another (Dexter or Forster transfers), until it reaches a dissociation site that allows the charge carriers to be separated. In the presence of a junction, electrons are attracted to material with a high electron affinity and holes to material with a low ionization potential.

The separation requires an energy greater than the binding energy between the hole and the electron. This energy can be obtained by various processes: thermal excitation, presence of impurities, generated electric field and, depending on the structure, by the junction of two semiconductors of different nature and type (heterojunction), or by the potential barrier between a metal and a semiconductor (Schottky diode) ...

VI. 3. Transport and collection of charges

The freshly created charge carriers join the electrodes and the external circuit of the cell.

Charge transport is controlled by the mobility of the carriers in the organic layers.

VII. SOLAR TECHNOLOGIES BASED ON ORGANIC MATERIALS AND OPERATING PRINCIPAL

The third generation appeared in the 1980s, and includes technologies based on organic materials. This technology is still in the development phase and seeks to combine low-cost production from abundant materials with high yields. Originating from chemistry, organic materials are cheap and can be obtained in large quantities. The properties of these materials can be modified according to the application and design chosen. In addition, they can be processed from solutions using continuous manufacturing processes such as roll-to-roll and inkjet processes. This is a definite advantage compared to inorganic panels.

These new technologies can be classified into:

- Schottky cells (monolayer structure)
- Two-layer heterojunction cells
- Volumetric heterojunction solar cells
- Solar cells based on perovskite absorbers
- Dye solar cells

VII. 1. Mono-layer structure / Schottky cells:

Consists of an organic film deposited between two metal electrodes (p or n type semiconductor). The indium tin oxide ITO is often used for the anode and a metal with a lower work function than ITO such as Al, Ca or Mg for the cathode. The choice of metals is decisive for making an ohmic contact on one side of the organic material and rectifying on the other side. The active area for the photovoltaic conversion is between one of the electrodes metals and semiconductor.

The electric field generated at the blocking interface forms a potential barrier. This barrier is responsible for the dissociation of the excitons. If the exciton is created near the ohmic interface, it must pass through the entire thickness of the material to reach the dissociation site. However, the exciton scattering length is small, in the order of 5 to 30 nm in common organic materials.

Regardless of the organic materials used and the nature of the electrodes, conversion efficiencies remain low. The low performances obtained with the Schottky structure are mainly due to the low mobility of the charge carriers as well as to the strong electron-hole interaction of the organic materials which limits the charge separation.

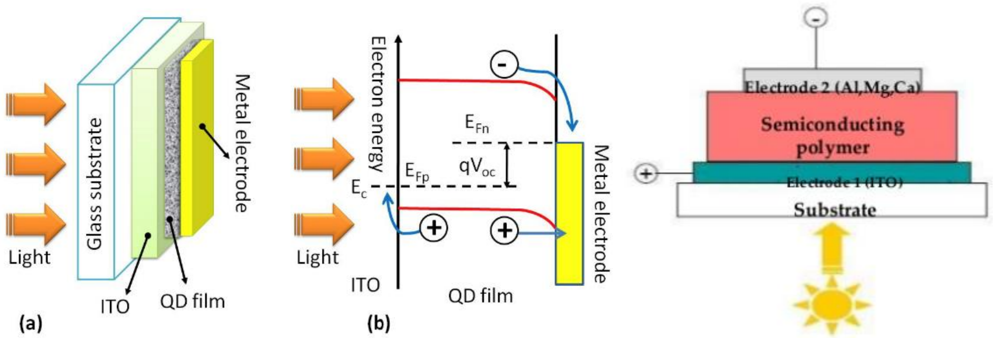


Figure II-4: Structure of a Schottky type cell and representation of contact energy levels.

VII. 2. Two-layer heterojunction cells/ heterojunction or PN:

The bilayer structure is composed of two materials of different natures (electron donor and electron acceptor) placed in contact between two electrodes. (**FigureI-5)**

The ITO is often used as a semi-transparent anode because it presents, on the one hand, a high transparency in the visible and, on the other hand, a moderate output work that can allow the establishment of an ohmic contact with certain hole-transporting materials. The cathode is rather made of metals such as aluminum or silver, which provide ohmic contact with certain types of n-type materials **[2] [3].** The two organic materials contribute to the generation of photocurrent with maximum efficiency, which is located at the interface between the two organic layers.

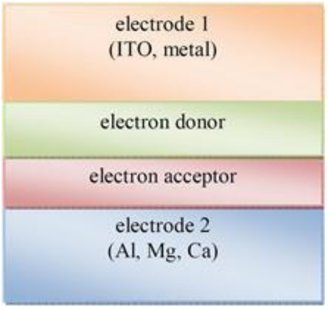


Figure II-5: representation of a two-layer heterojunction cell

In this case, the active area for the photovoltaic conversion is found at the interface between donor and acceptor. The electric field created at this interface is due to the difference between the ionization potential of the donor and the electronic affinity of the acceptor, as well as to the internal potential induced by the difference in the output work of the electrodes used. It allows the dissociation of the excitons that reach this site. Thus, the free charges will migrate separately to their respective electrodes: the electrons by the acceptor to the cathode and the holes by the donor to the anode.

Unlike Schottky type monolayer cells, this cell has a better spectral match to the spectrum of the sun. A significant improvement in the efficiency of bilayer cells compared to monolayer cells is interpreted by a more efficient dissociation of the excitons at the interface where there is a strong electric field. However, the disadvantage of this system is that it has a surface area of limited contact between the donor and the acceptor, which implies that the number of dissociated excitons will be limited. During photon absorption, the exciton formed must migrate to this interface (to be able to dissociate and generate loads). But, the scattering length of the exciton is generally in the range of 5 to 20 nm **[4],** thus only the excitons created at this distance from the interface will be able to dissociate, which limits photoconversion yields.

VII. 3. Volumetric heterojunction solar cells/ Interpenetrating network structure:

Today, despite published advances in the optoelectronic and structural properties of p/n heterojunction organic cells, their efficiency remains low. The main factor limiting this yield is not yet well defined. Some attribute it to the short diffusion lengths of the excitons in these materials. In this case, only a small thickness close to the organic/organic interface participates in the generation of the photocurrent. Other considered that the low values of the mobility of charge carriers are responsible for recombination before they are collected at the electrodes.

A new type of cell containing the donor and acceptor (volume heterojunction) was therefore developed **(figure I-6)**. to reduce the distance, the carriers have to travel to reach the electrode, and to limit carrier recombination. In addition, the increase in the surface area of the the p/n junction will improve the performance of the device. This structure consists of a composite layer of donor and acceptor deposited between two electrodes; this lattice has a phase separation on a scale smaller than the scattering distance of the exciton. The main advantage of this structure is that the mixing of the two materials makes it possible to multiply the interfacial zones between them and thus reduce the problems of losses by recombination of photogenerated excitons far from the interface (biomolecular recombination).

The photovoltaic effect here is generated by a photoinduced electron transfer from a conjugated polymer of donor type to a conjugated polymer of acceptor type or an acceptor molecule, all contained in a single active layer **[5].**

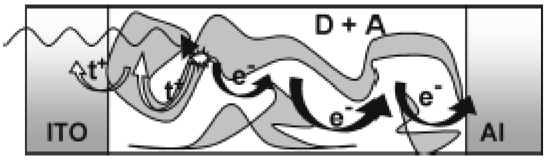


Figure II-6: volumetric heterojunction cell structure

VII. 4. Solar cells based on perovskite absorbers:

These cells are based on an inorganic/organic hybrid material which is defined by its crystalline structure called "perovskite". Its general formula is ABX3 where A is an organic cation, B is a divalent cation and X is a halide anion.

The efficiency of these cells is close to that of monocrystalline silicon cells 25% **[2].** In addition to the high yield, these cells are relatively easy to manufacture, the base materials are cheap and available in large quantities and the absorption coefficient of perovskite crystals is higher than inorganic technologies.

The major problem with these devices is their stability over time, which is much lower than that of inorganic panels.

VII. 5. Dye solar cells:

Inspired by photosynthesis, the dye-sensitized solar cells (often referred to in the literature as DSSC), or the Grätzel cells, named after their designer. These hybrid solar cells are composed of a mesoporous photo-anode consisting of a layer of wide-gap inorganic semiconductor (usually TiO2) sensitized with an active molecule (the dye) that is organic or organometallic. The cell is sealed with a counter electrode while the cavity between the two electrodes is filled with a liquid electrolyte. (**Figure I-7)**

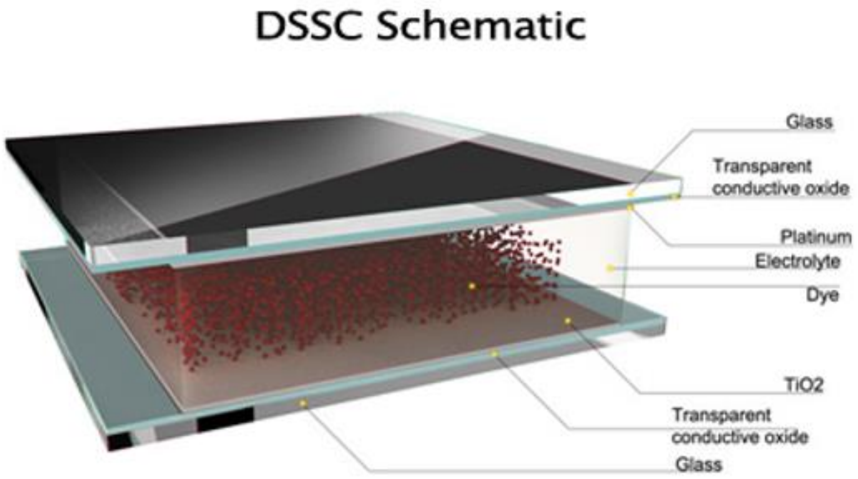


Figure II-7: *DSSC schematic*

DSSC have a different functioning than the one described above (**figure06)**. The functions of photon absorption and charge transfer are differentiated; the light-absorbing part is a dye (called S-sensitizer) located at the interface between an n-type semiconductor (SC) (titanium dioxide TiO2) and an electrolyte (redox system, usually I-3/I-). At the absorption of a photon, the sensitizer goes to the excited state (S0 → S*) and is able to inject an electron into the conduction band of the n-type SC. The injected electron passes through the SC layer to reach the external circuit and generate the current. The sensitizer (then in the S* form) returns to its fundamental state by hole/electron exchange with the redox system which oxidizes. The redox system then gives its charge to the counter-electrode, which allows it to return to its ground state as well.

The operating cycle can be summarized in the following chemical reaction terminology:

Anode: $S + h\nu \rightarrow S^*$ *Absorption*

$S^* \rightarrow S^+ + \acute{e}\,(TiO_2)$ *electron injection*

$2S^+ + 3I \dashrightarrow 2S + I_3^-$ *regeneration*

Cathode: $I_3^- + 2\acute{e}\,(pt) \dashrightarrow 3I^-$

Cell: $\acute{e}\,(pt) + h\nu \dashrightarrow \acute{e}\,(TiO_2)$

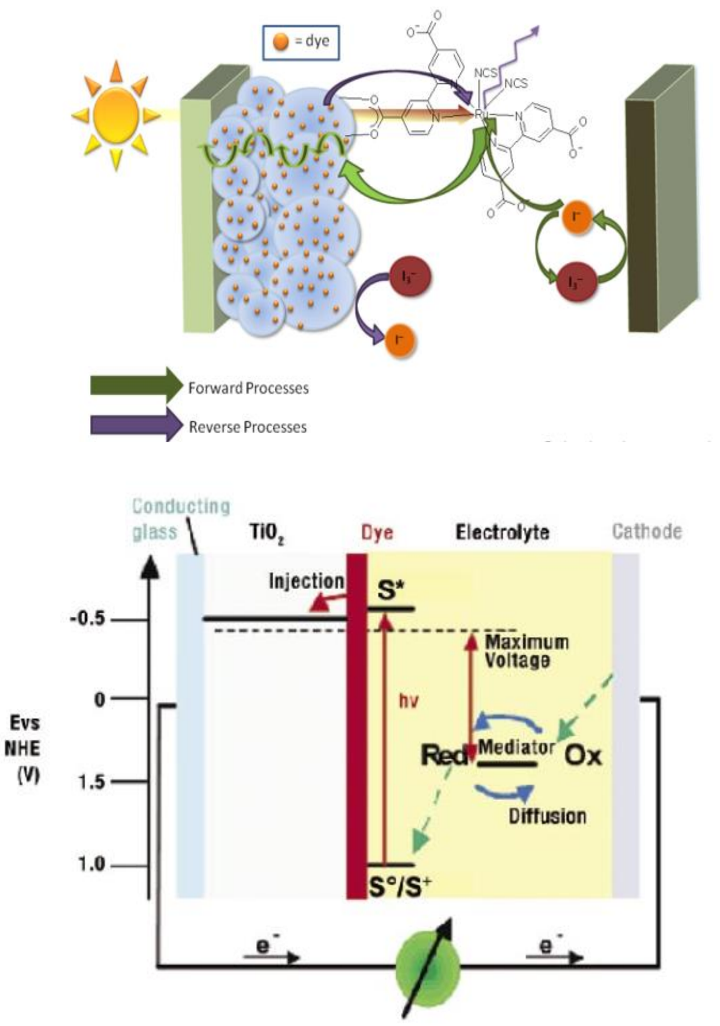


Figure II-8: functioning process of the DSSC

The main characteristic of these devices is that they are semi-transparent and colored depending on the sensitizer used. They work even under low illumination or diffused light. In addition, dye-sensitized solar cells do not use expensive materials and are fairly easy to produce, although it should be taken into account that this sector does not benefit from a market as developed as that of silicon and that a reduction in costs is expected if this technology is developed with the implementation of more efficient production tools. Compared to inorganic panels, dye cells can be oriented vertically without a precise angle and do not lose efficiency. This advantage is due to the transparent structure of the electrode and the diffusing ability of the oxide layers to reflect non-absorbed light back to the photoactive species. The structure of these electrodes will be detailed later in this chapter.

Currently, efficiencies in excess of 11% (under standard AM1.5 illumination conditions) have been obtained from cells using ruthenium complexes as a dye **[6].** Because of the high cost of ruthenium complexes but also their toxicity, some groups are working on the development of metal-free organic dye cells. These cells develop yields of 5 to 8%.

In carrying out our work, we have taken a particular interest in this structure. The following titles are devoted to the detailed study cells based on organic dyes.

VIII. DYE-SENSITIZED SOLAR CELLS

VIII. 1. Main components:

Grätzel type cells consist of two conductive glass electrodes: the photo-anode and the counter electrode, a photoactive molecule, a hole conducting material and a counter electrode. **Figure07**

- The photo-anode includes a metal semiconductor oxide layer deposited on a transparent conducting oxide (TCO) on a glass substrate or on plastic substrate.
- The photoactive molecule anchored to the mesoporous oxide semiconductor is a dye molecule which has the ability to harvest solar light.
- It is surrounded by a hole conducting material in the form of liquid electrolyte containing a redox shuttle or as a solid hole transporting material (HTM: hole transporting material).

Each component of the cell has an influence on the conversion efficiency. Each change in a component induces a change in performance and a lot of research has been carried out in this direction. This is why it is important to detail its different components.

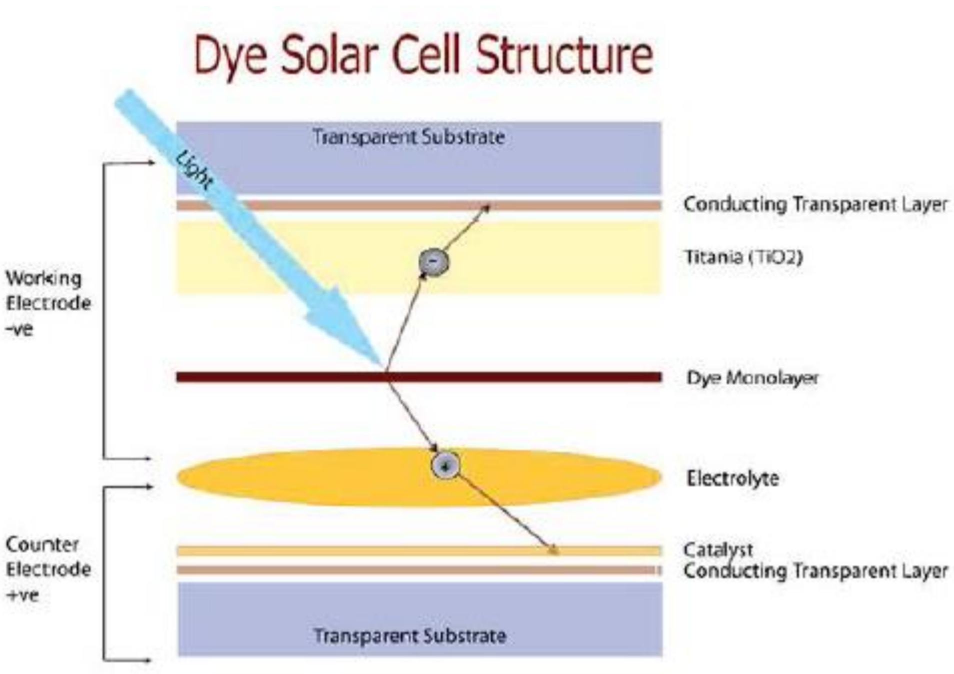


Figure II-9: *Composition of a Grätzel-type solar cell*

VIII. 1. 1. *The photoanode*

It is the first component of the device. It must be rigid enough to support the active layer. It must also be conductive while maintaining high light transmittance. It must be able to withstand the heat treatments necessary to manufacture the electrodes and must be able to contain the liquid electrolyte.

For many years, two conductive oxides have been used in electronic devices. Fluorine-doped tin oxide (FTO for "Fluorine Tin Oxide") and tin-doped indium oxide (ITO for "Indium Tin Oxide").

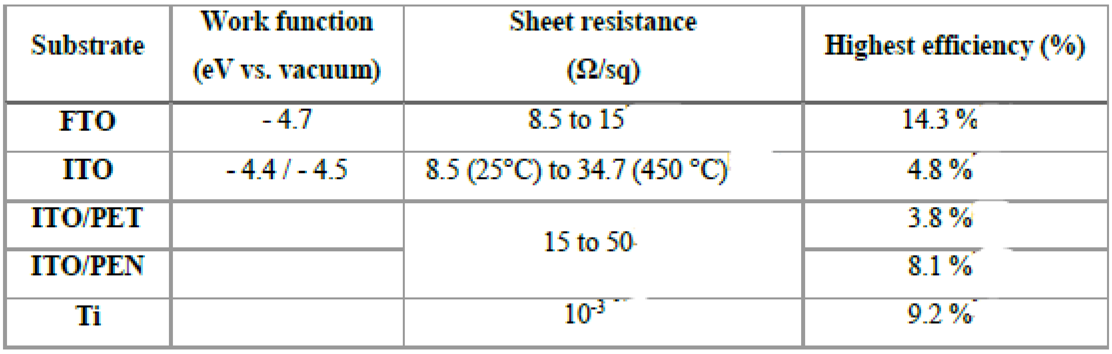
VIII. 1. 1. 1. Transparent Conducting Oxide (TCO):

Among TCO supporting glass substrates in DSSC, fluorine doped tin oxide (FTO) is widely privileged compared to indium doped tin oxide (ITO), due to its electrical and optical properties, its stability at high temperature and its cost. This n-type semiconductor, characterized by a large direct bandgap of 4.1 eV, has a transmittance higher than 80 % in the visible range.

These two TCO were investigated on DSSCs by respectively C. Sima and al. obtaining an efficiency of 2.24 % and 9.6 % for ITO and FTO **[11]**

For more extensive DSSCs applications, flexible substrates such as plastic or metal have been developed. Usually for plastic substrate, polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) coated on indium tin oxide (ITO) are used whereas titanium foils or stainless-steel foils are applied for the preparation of metal substrate. Besides their flexibility, lightweight and production cost, plastic/ITO and metal substrates are not as conductive **(Table 1**) and transparent as FTO and the sheet resistance decreases dramatically with the temperature **[12].**

Tableau II-1: *Electrical parameters of TCO and metal substrate and the highest efficiency obtained for DSSC using these materials as photo-anode substrate.[13]*



Substrate	Work function (eV vs. vacuum)	Sheet resistance (Ω/sq)	Highest efficiency (%)
FTO	- 4.7	8.5 to 15	14.3 %
ITO	- 4.4 / - 4.5	8.5 (25°C) to 34.7 (450 °C)	4.8 %
ITO/PET		15 to 50	3.8 %
ITO/PEN			8.1 %
Ti		10^{-3}	9.2 %

VIII. 1. 1. 2. Metal Oxide Semiconductor

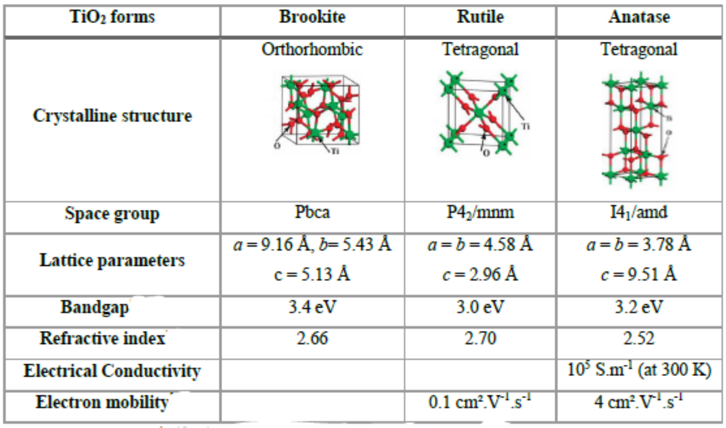
The metal oxide semiconductor that supports the photoactive molecules should be, at first, an n-type semiconductor to transport electrons with a wide bandgap Energy (EG > 3 eV) and must be transparent to the major part of the solar spectrum and with a low light scattering effect. In order to act as an electron acceptor, the CB (conduction band) energy level of the semiconductor should match with respect to dyes excited state. The metal oxide semiconductor should have a large surface area for a maximum dye adsorption and should be highly porous and conductive **[13].** Different metal oxides have been investigated such as SnO2, Al2O3, Nb2O5 and SrTiO3 which show a bandgap higher than 3 eV. Typically, TiO2 and ZnO are the most investigated oxides owing to their attractive electronic properties depending on the morphology and the crystal structure.

VIII. 1. 1. 3. TiO2*:*

The most common semiconductor used in dye-sensitized solar cells is titanium dioxide (TiO2). We have chosen to focus only on the properties of TiO2 as a semiconductor. Titanium dioxide is non-toxic, has a high refractive index, it is commonly used in paints, sunscreen or toothpaste as a white pigment and is found in our food as an additive under the abbreviation E171 (titanium dioxide).

Titanium dioxide is present in nature in three forms: rutile which is the thermodynamic form, anatase and brookite. Anatase is the form used in Grätzel-type cells. TiO2 crystallographic characteristics and physical properties are given in **Table 02**.

Tableau II-2*: TiO2 crystallographic characteristics and physical properties [12]*



TiO_2 forms	Brookite	Rutile	Anatase
Crystalline structure	Orthorhombic	Tetragonal	Tetragonal
Space group	Pbca	$P4_2/mnm$	$I4_1/amd$
Lattice parameters	$a = 9.16$ Å, $b = 5.43$ Å $c = 5.13$ Å	$a = b = 4.58$ Å $c = 2.96$ Å	$a = b = 3.78$ Å $c = 9.51$ Å
Bandgap	3.4 eV	3.0 eV	3.2 eV
Refractive index	2.66	2.70	2.52
Electrical Conductivity			10^5 $S.m^{-1}$ (at 300 K)
Electron mobility		0.1 $cm^2.V^{-1}.s^{-1}$	4 $cm^2.V^{-1}.s^{-1}$

The use of TiO2 electrodes has led to conversion efficiencies in excess of 13% mainly through a research effort focused on the dye or electrolyte that will be developed later. The greatest disadvantage of titanium dioxide is its low electron mobility (0.1 cm2V-1s-1) which does not allow very efficient charge removal.

VIII. 1. 1. 4. ZnO:

As for TiO_2, ZnO is a white pigment used in paint, food, ceramic, glass, cements … It is also applied as n-type semiconductor in DSSC using a wurtzite-type crystalline structure, the most thermodynamically stable structure. Wurtzite ZnO has a wide direct bandgap of 3.37 eV with a similar conduction band edge, work function (W) and refractive index as compared to TiO_2, but with a higher carrier mobility allowing an efficient electron transport: key factor that impact the overall efficiency. Furthermore, ZnO synthesis can be carried out under softchemistry conditions (low temperature). This opportunity offers promising prospects to flexible DSSC applications**.** **[12]**

Titanium dioxide and zinc oxide are two materials with similar electronic properties. With a similar bandgap and conduction band (**Table 3**), ZnO differs from its counterpart mainly by its much higher electron mobility (two orders of magnitude higher), and its diversity of accessible nanostructures. Currently, the best conversion yield obtained with zinc oxide was reported by Memarian et al in 2011 with 7.5% **[15].** The different strategies for improving ZnO-based devices have not allowed to surpass this record because of the low chemical stability of ZnO which is mainly due to the basic properties of the oxide (pH=9), and the low injection rate of the photo-excited electron into the ZnO conduction band.

Tableau II-3:*Summaries of the properties of various semiconductor oxides.*

Oxyde	E_g (eV)	μ_e ($cm^2V^{-1}s^{-1}$)	E_{CB} (eV vs vacuum)	Point isoélectrique (pH)	η_{max} (%)
TiO_2	3,20	0,1-1	-4,0	6-7	14,6%[73]
ZnO	3,35	100-300	-4,1	9	7,5%[72]
SnO_2	3,80	100-200	-4,5	4-5	9,5%[74]

VIII. 1. 1. 5. Blocking layer:

In both TiO_2 and ZnO, a dense blocking layer or underlayer is required to prevent any contact between the TCO and the hole conducting material that diffuses through the semiconductor mesopores. The blocking layer is able to reduce charge recombination, to enhance the suppression of current leakage, to increase the open circuit potential (Voc). The thickness is well monitored to ensure the conductivity and not the resistivity. Usually the thickness is between 10-100 nm which has demonstrated a significant improvement in device functional performances. **[12]**

VIII. 1. 2. *Th dye*

The photo-sensitizer or dye is a crucial component actively involved in light absorption, in light harvesting, in charge separation, and in the electron and hole injection into the oxide semiconductor and into the hole conducting material respectively.

There are two types of photosensitizers, organometallic dyes and organic dyes. Organic photosensitizers are the most attractive candidates, owing to their high molecular extinction coefficient, their low production cost, their easy and versatile synthesis and their wide variety for the molecular structure design as well as their pleasing range of colors across the visible spectrum, from deep red to violet. The other advantage of these molecules is that the optical and electrochemical properties can be modulated by changing the chemical structure of the compound. The addition of chromophores will have an influence on the spectral absorption range but also on the energy levels. By combining these two advantages, a wide variety of strategies and compounds can be implemented to obtain effective dyes. In terms of performance, organic dyes have progressively caught up with the organometallic dyes with a yield of 13%.

The dyes must have a function that allows the photosensitizer to be grafted onto the surface of the semiconductor. Three functions are commonly used in the literature, carboxylic acid (-COOH), phosphonic acid (-H2PO3); sulfonic acid (-SO3H) **[16].** The anchoring of the dyes can be done in covalent or non-covalent ways. Covalent bonds are sought because they prevent the dyes from desorbing in the cell**. [17]**

In addition, the dye must have maximum absorption in the visible range. The photosensitizer must also have a higher oxidation potential than the redox mediator of the electrolyte in order to be reduced. The structure of the dye must prevent the phenomena of aggregation and stacking of molecules so that the electron diffuses into the conduction band of TiO2 even if the use of an additive (chenodeoxycholic acid) can be used to move the dye molecules away during grafting**. [18]**

Finally, the synthesis of this dye must be reproducible, using if possible cheap products with only a few synthesis steps.

VIII. 1. 3. ***The electrolyte***

The electrolyte is made up of an oxidant/reducing couple which acts as a mediator in the cell and various additives which allow the interactions inside the cell to be optimized. Electrolytes have mixtures of additives in their compositions for optimizing the performance of electron charge transfer in the conduction band by reducing parasitic reactions.

There are also electrolytes in gel or polymer form. Electrolytes in the form of gels or polymers come from liquid electrolytes or ionic liquids that have been gelled, polymerized, or dispersed in polymeric materials. Load transfer is achieved by diffusion. The proportion of redox torque is increased due to the viscosity of the medium and the reduced mobility of the charges. This limitation of mobility of the redox mediator leads to a decrease in the photovoltaic performance of the cell.

The type of electrolyte used will influence the photoelectric properties of the cell and its photovoltaic performance.

The electrolyte must have different properties **[2]:**

- The solvent must have a low melting point (-20°C) and a high boiling temperature (>100°C) to avoid evaporation under conventional conditions of use (between -10°C and 70°C outdoors).
- It must also have a large electrochemical window guaranteeing the chemical stability of the species present in solution in the range of use of the cells under illumination.
- In order to guarantee good conduction in the case of electronic equipment, the solvent must have a high dielectric constant allowing total dissociation of the salts and their solubilities.
- It must also have a low viscosity allowing a good diffusion of redox species in solution.
- Compounds present in solution must not have a chemical reactivity with the electrode or dye that could lead to degradation of the cell. The absorption of these molecules must not impair the absorption of the dye.
- Finally, the redox potential of the redox couple must be correctly placed in relation to the HOMO energy level of the dye.

The oxidizing-reducing couple is the electrochemically active species. The most commonly used couple is the Triiodide/Iodide (I_3^-/I^-) couple with an oxidation-reduction potential adapted to the majority of the dyes studied.

VIII. 1. 4. *Counter electrode*

The counter electrode (CE), adjacent to the redox mediator is the last element that completes the internal electrical circuit of a DSSC. The counter-electrode plays an equally important role as the photoanode. Two roles are attributed to this element:

i. Regeneration of the oxidized form of the redox couple to regenerate the reducing species necessary for the regeneration of the dye.

ii. It must also evacuate the holes to the external circuit efficiently to avoid any loss of charge.

The counter-electrode is covered on its conductive surface (FTO) with a thin layer of platinum nanoparticles which will allow the diffusion of electrons towards the redox mediator of the electrolyte which will be reduced. This platinum layer is obtained by the reaction at hot temperature of a precursor deposited on the surface (drop by drop or spread with a brush).

There are also other substrates such as titanium or NiP/glass coated with Pt, which have the advantage of increasing the efficiency by light reflection and by decreasing the series resistance.

All this can be summarized in the following table:

Component	definition/characteristics	used materials	Role
Substrate	These are usually coated TCO (transparent conducting oxide)	- Fluorine-doped tin oxide (FTO) - Indium tin oxide (ITO)	The substrate serves as a supporting structure for the cell and acts as a sealing layer.
nanostructured electrode	They are generally based on an oxidized semiconductor because of its stability against photo-corrosion during optical excitation of the gap.	TiO2 (Most used), ZnO, CdS, Fe2O3 ...	-Thanks to their wide gap (3eV), oxidized semiconductors allow to have transparent electrodes in order to collect the largest possible part of the solar spectrum. - They serve as collectors of electric current

sensitizing dye	These are specific dye molecules placed on the surface of the semiconductor electrodes.	-The general structure is : ML2 (X)2 Example : - Cis -RuL2 (NCS)2	- They perform the function of an electron pump.
Electrolyte	The electrolyte used in DSSCs consists of a redox couple in an organic solvent with the possibility of finding other substances to improve the performance of the cell.	- for the redox couple : I^-/I_3^- - For the solvent: acetonitril, methoxyacetonitrile, ethylene carbonate ...	- They are used to transport the holes. - They are also used to reduce the molecules of oxidized dye after the injection of electrons.
counter-electrode	These are the electrodes on the side opposite the cathode (the nanostructured TiO2 electrode).	- Generally, the Platinum (Pt) is used exclusively. - The carbon (C) (cheaper than pt) is piercing through	-It is used to collect the holes -They also serve as a catalytic coating for a rapid triiodide reduction reaction at the TCO cathode.

VIII. 2. Operation principal

Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at the p-n junction of the SC (solar cell). Electrochemical photo cells are operated in such a way, the light absorption processes are separated from the processes of charge separation. The principle of operation of these photovoltaic cells is inspired by the phenomenon of photosynthesis in plants.

A charge separation within a dye excited by absorbed solar energy creates an electron-hole pair whose separation and transport induces a current by their movement in the external circuit. The sensitizing dye is grafted onto the surface of a nanostructured porous semiconductor oxide in the form of a monomolecular layer. It absorbs the incident solar rays which cause it to enter an electronically excited state where it is able to inject an electron into the conduction band of the semiconductor TiO^2. The injected electrons pass through the semiconductor layer and are then collected by a current collector. The regeneration of the dye in the neutral state is carried out by means of a redox system introduced in solution in the liquid electrolyte. The ion of the redox system will reduce the oxidized dye and the charge transfer in the electrolyte is then done by electron jump from an oxidized site to a reduced site. The return of the electron (transferred to the TiO^2) into the valence band (HOMO) of the oxidized dye (recombination) is much slower than the electron transport in the TiO2. This allows efficient charge collection. Finally, the iodine formed is reduced at the counter electrode.

The mechanism mainly occurs in 6 steps as the following **[12]:**

Light harvesting of dyes for charges carrier generation:

From sunlight, the incident photon is absorbed by the photosensitizer and thus promotes an electron from the HOMO (Highest Occupied Molecular Orbital). To the LUMO (Lowest Unoccupied Molecular Orbital) level **(figure08):** the dye which was initially in the ground state **D** is now in an excited state **D***.

$$\mathbf{D + h\nu \rightarrow D^*}$$

Electron transfer toward the oxide semiconductor:

The photo-excited sensitizer **D*** injects the electron into the conduction band of the semiconductor leaving behind a hole: the sensitizer is in oxidized state $\mathbf{D_+}$.

$$\mathbf{D^* \rightarrow D_+ + e_- (CB_{TiO2})}$$

Electron transport across the photo-anode:

The electron in the conduction band flows through the oxide semiconductor toward the TCO of the photo-anode and then conveyed to the external circuit until the cathode.

Regeneration of the oxidized dye by electron transfer:

The oxidized dye $\mathbf{D_+}$ returns back to its ground state **D** through the electron injection from the electron donor or reduced species of the redox mediator from liquid electrolyte, or from the HTM (Hole transporting material). The reduced species are thus oxidized.

$$\mathbf{D_{+} + Red \rightarrow D + Ox}$$

$$\mathbf{D_{+} + HTM \rightarrow HTM_{+} + D}$$

Hole transport across the hole transporting layer:

In the case of liquid electrolyte DSSC, the oxidized species diffuse progressively toward the counter electrode whereas for HTM, the received hole from oxidized dye roams along the HOMO level as “hopping” process until the counter electrode.

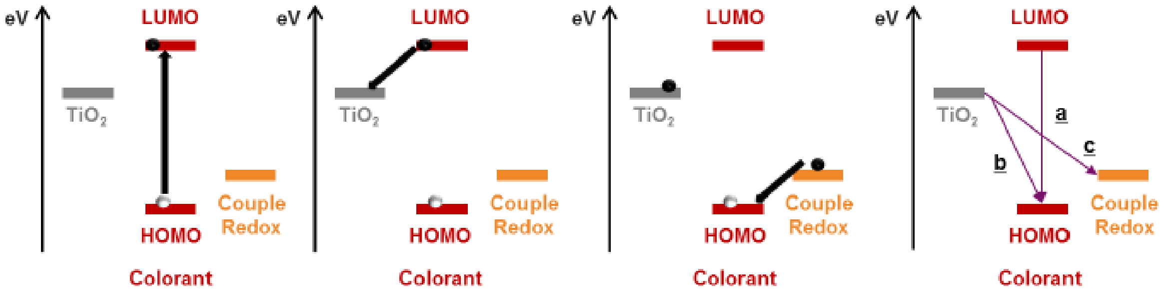
Hole transfer or reduction at the cathode:

The oxidized species are reduced back thanks to the counter electrode.

$$\mathbf{Ox + ne_{-} \rightarrow Red}$$

$$\mathbf{HTM_{+} + e_{-} \rightarrow HTM}$$

The cycle is therefore completed. However, the device will operate only if the reaction kinetics takes place for the different interfacial electron transfers.



Photon absorption Injection Re-generation Recombination

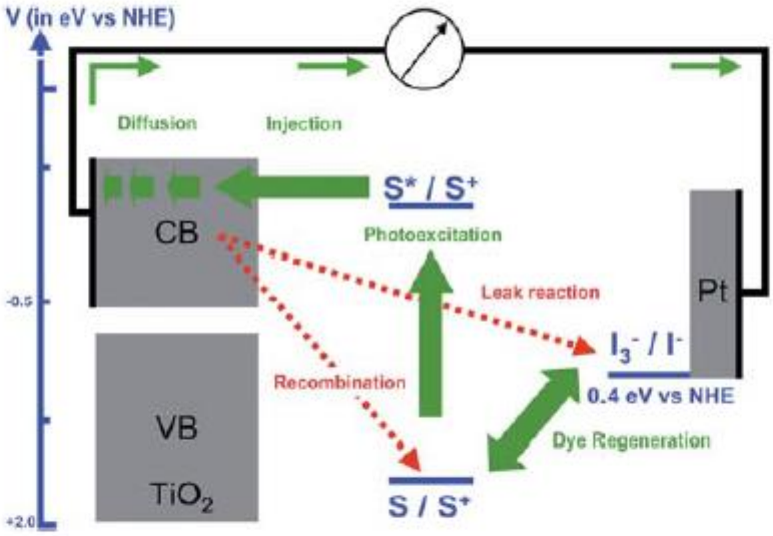


Figure II-10:*Physical principle of operation of a dye-sensitized solar cell.*

VIII. 3. Analogy with Photosynthesis

In contrast to conventional silicon-based cells, the operating principle of dye cells is based on the natural process of the Photosynthesis; i.e. the processes of light absorption and charge separation are differentiated and carried out by different materials. Each molecular component performs only one function for which it is optimized.

Figure II-11: *Analogy between Photosynthesis and photovoltaics*

VIII. 3. 1. *Photosynthesis [4]*

Photosynthesis t exists in plants and in certain bacteria (cyanophycean). It is made possible by a series of biochemical reactions driven by light as an energy source, involving simple mineral molecules (CO_2, H_2O...), produces organic carbohydrate molecules of relatively low molar mass. It is nothing more than an oxidation-reduction reaction between water, the reductant, and carbon dioxide, the oxidant.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Photosynthesis is a process in which abundant and ephemeral light energy is captured and converted into chemical energy in the form of an energy storage molecule (ATP) to meet the present and future needs of the organization. This process can be broken down as follows:

- the photon is captured by a biological antenna, well anchored in the membranes of small “Photosynthesis pockets" located inside the cells, the chloroplasts (a plastid in green plant cells which contains chlorophyll and in which Photosynthesis takes place)
- This antenna performs an energy transfer and sends the photon's energy into another large molecule of the chloroplast membranes, the reaction center: this is where the electromagnetic energy is transformed into an electron-hole pair, thanks to an electron transfer. A dimeric entity at the reaction center, composed of "porphyrins", receives energy from the antenna and, excited, injects an electron to another porphyrin further away.
- From there, the electron travels in successive transfers. In doing so, it moves away from the positive hole left at its departure, in order to avoid recombination. The hole, also ends up moving away and transforming itself.
- In the end, the photon sent by the Sun creates in the chloroplast a negative charge and a positive charge very far from each other, distributed on both sides of the chloroplast membrane. They are taken care of by other very complex biological mechanisms; their role is to store chemical energy in a less fragile and less ephemeral form, ATP.

VIII. 3. 1. 1. Analogy with Photosynthesis:

The photovoltaic cell is the base element constituting a photovoltaic module, which can convert solar energy into electrical energy by the photovoltaic effect.

The Photosynthesis is an endothermic process that occurs in factories and in a certain organization and thanks to unicellular solar energy is transformed in chemical energy, included in glucose molecules and in the bond of other organic substances.

The Grätzel cell, in its functioning, refers to Photosynthesis:

- It uses an organic dye equivalent to chlorophyll to absorb light and produce electron flow.
- It uses multiple layers to improve the efficiency of light absorption and electron gathering.
- Both systems use exciting electron photons by the collection on a flat surface: the leaves and solar cells.
- Plants have the DNA that allows them to perpetuate the self and reproduce, PV systems do not.
- Photovoltaic systems have an average lifespan of about twenty years, while plants can actually grow anywhere from one year to more than four thousand years.

Both plant and solar cells must handle excited electrons quickly, before they give up their energy and go back where they were before they absorbed their photons. In Photosynthesis, the problem is solved by moving the electron from one molecule to another until it settles in a molecule that can store energy for a long time. In photovoltaics the excited electrons are whisked off into a circuit **[19]**

IX. ADVANTAGES OF PHOTOSENSITIZED OXIDE SOLAR CELLS

The cells based on photosensitized oxides have several advantages over conventional silicon-based photovoltaic cells.

First of all, the oxides n-type semiconductors such as TiO_2, SnO2 or ZnO are inexpensive, abundant, and have low toxicity. On the other hand, the silicon used in photovoltaic cells has to be very pure, which significantly increases production costs.

Moreover, unlike conventional cells, the functions of creating electron-hole pairs and electron transport are clearly separated in this type of cell, since, after injection, the electrons are in the oxide while the holes are located on the chromophores. These characteristics therefore make it possible to limit certain recombination processes.

Furthermore, when silicon cells are illuminated at an oblique angle, there is a lot of reflection, which affects the efficiency of cells. On the contrary, oxide-based cells reflect much less sunlight, as the thickness of the layer through which it passes and the absorption increases.

These cells are stable up to temperatures of 60°C and their semi-transparent nature makes them aesthetically pleasing. In addition, they have sound and heat insulation properties that are particularly interesting for applications in buildings.

X. A NEW DESIGN

How do you get the solar cells off their roof panels? How to integrate them in everyday objects? To answer these two questions, we propose 3 surprising projects that have been completed and exhibited at the Ecole Nationale Supérieure de Création Industrielle in Paris.

X. 1. Insect Killer

Students from the Royal College of Art (RCA) in London have taken as a starting point to their projects of existing objects, which were already powered by solar energy. They thus examined clocks, lights, calculators, battery chargers or mosquito repellent. The latter proved to be particularly not well conceived: it took two days to charge it, then one day only to deplete its energy.

From this thought was born, among others, the insect killer. A project of Ming Kyu. In order to solve the problem which constituted the starting point, this project has divided the tasks: it only powers a UV diode, which attracts insects, and lets a carnivorous plant do the rest. Can you imagine anything simpler?

***Figure II-12**: Green insect killer*

X. 2. Hang

The author of the Hang project, Georges Moanack, started with a solar torch. Problem: to be operational, the object had to be exposed to light for a long time. But a torch, when you don't use it, put it aside and not necessarily in the sun.

The student then thought of the Do not disturb, those little signs that you hang on the doors of the hotel rooms. And decided to make ends meet: his torch takes the shape of the little panel alarm of hotels and thus turns into a night light for the children's room.

***Figure II-13**: the project hang*

X. 3. Electrifier

A particularly original idea flourished at the National Higher School of Industrial Creation (ENSCI) in Paris. It is a wall support that allows decorative, aromatic or medicinal plants to grow inside the home.

The designer of this project, Alexandre Kournwsky, explained that he wanted to use the beneficial effect of electricity on plant growth and quality. Thus, his Electrifier unrolls like a ribbon and hangs on the wall. After cutting openings in his batyline skin, strips of pre-sown seeds are inserted. The plants then take root in a hydrophilic substrate that propagates the water, which is poured into a reservoir. Electrical stimulation comes from solar cells embedded in the side of the object and is transmitted to the roots by means of a solar cell to two structural grids.

Figure II-14: *Electrifier*

XI. LIMITATIONS AND DIFFICULTIES TO OVERCOME

The main sources of efficiency loss are related to the recombination phenomena of the photoelectrons. Losses are also due to the reflection and absorption of light by the transparent conductive glass used as a substrate**.** There are various recombination mechanisms that decrease the yield. As the films are porous and therefore have a large specific surface area, the photoelectrons present in the semiconductor oxide can recombine either with the oxidized dye or with the redox mediator**. [20]**

The dye can also be de-excited before the electron is injected into the CB of the oxide by radiative (fluorescence) or non-radiative (quenching) means**. [21]**

The recombination reaction of the photoelectrons with the oxidized dye is negligible for TiO2-based cells. Indeed, the recombination with the oxidized dye is slower than the redox reaction with the mediator. Injection times are of the order of (10 -13 s) whereas recombination phenomena take place over several microseconds.

These ultra-fast injection times are also much faster than the dyestuff de-excitation times. The greatest source of recombination is the interaction between the photoelectrons and the oxidized mediator. The regeneration of the oxidized mediator is governed by its diffusion to the cathode, which is a slow mechanism. Recombination with the mediator occur on the surface of the particles.

In order to reduce this recombination, it is necessary to increase the load separation space. Different approaches have been explored in this context. First of all, core-shell structures with two oxides, have been developed. This type of core-bark structure allows the creation of a barrier, this barrier increasing spatial separation, modulating the dipoles and passivating surface finishes, recombination centers. **[22]**

In addition, the addition of lithium ions adsorbed on the surface of the oxide allows the injected electrons of the oxidized mediator to be skimmed off. In addition, these basic additives will increase the CB of the oxide, increasing the open circuit voltage. On the other hand, the current decreases since the injection is less effective**. [23]**

It is obviously necessary to limit recombination, on the one hand to increase the quantum efficiency and therefore the output current and, on the other hand, to increase the open circuit voltage.

XII. CONCLUSION

In the field of new technologies for energy, organic photovoltaic solar is becoming an industrially strong axis of development now that there is a desire to reduce fossil energy consumption and greenhouse gas emissions. In this context, basic research is essential to validate and demonstrate the interest of this sector for a decisive reduction in costs and to remove the various technological obstacles identified to date.

While silicon, whether single-crystalline or amorphous, has been the most widely used material for the manufacture of photovoltaic cells, organic solar cells have many advantages over conventional solar cells. Unlike silicon, whose production requires very high temperatures, their manufacturing involves low nanoscale, energy costs and low environmental impact.

If today the yields obtained with organic cells are far from competing with inorganic solar cells, accelerating research and innovation could rapidly make the organic ivy viable. The race for yield is launched between different teams of researchers from all over the world. With the aim of improving the performance of organic cells, many materials and Various architectures have been developed.

DSSC technology still has a long way to go out and catch up with nature. DSSC technology is based on the process by which plants transform light into energy and store it. Plants that use photosynthesis operate 24/7, even when the sun is not shining. Essentially, it's the work of these long hours that will turn out more efficient than silicon-based DSSC from solar cells. Bioinspired DSSC is more powerful in a wide range of conditions: light, temperature and its material flexibility, it is easy to integrate into a wide range of applications. DSSC will also be much less expensive than silicon based solar cells and will not leave the imprint of carbon emissions that today's solar power plants make. In short, the application of the existing DSSC technology and new materials will be revolutionary, in changing the way we interact with many of our environments.

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Chapter III : QSPR MODELING

I. INTRODUCTION

The experiment is a straight way to obtain data on the activity/properties of organic compounds. Most of the time, those experiments require a large experimental organism, cost a lot of money and are time-consuming, which makes them deficient to achieve. In addition to the difference between the values obtained by different researchers depending on the experimental conditions. Therefore, it would be impossible for the experiment to provide activity values for all organic compounds. It is crucial to use theoretical methods to compensate the disadvantages of the experiment and to predict the exact data (activities or properties) of the compounds.

The significant development of computer science as well as theoretical studies of quantum chemistry allow researchers to obtain more accurate physicochemical and quantum parameters of compounds in a shorter time. Structural parameters as well as the introduction of the quantitative structure-activity (or property) relationship QSAR/QSPR can increase the interpretation and predict the activity/property for new organic compounds.

These new modeling techniques have enabled the implementation of numerous QSPR methods (Quantitative Structure Property Relationships) and QSAR (Quantitative Structure-Activity Relationships), most of them are based on "finding a relationship between a set of numbers molecular descriptors, and the property or activity we wish to predict.

These methods are used to justify the available experimental data and to predict properties/activities for new compounds or compounds for which the experimental data are not available.

The QSAR/QSPR methods are based on the assumption that the activity or property of a chemical compound is related to its structure, specifically this approach states that the activity (or property) and structure of a chemical compound are linked by a certain mathematical algorithm, this is based on the basic postulate "similar chemical compounds have similar activities". [1]

In other terms, QSPR method is the study of the correlation between chemical structure and associated properties (physico-chemical), with the ultimate goal of predicting the properties of untested chemicals based on structurally related compounds with known activity. [2]

II. DEFINITION OF QSPR: [3]

The QSPR (Quantitative Structure- Property Relationships) is the process by which quantitative links are established between the molecular structures of a set of compounds with a physico-chemical property. The main development phases of a QSPR model can be described as follows:

- Choose descriptors appropriate to the structure-property problem,
- Exploit the values of the descriptors as variables, in order to define a relationship that correlates them to the property in question, using learning machines. This is the data mining.
- Establish performance and validation criteria that will assist in the selection of the best models for the problem posed and estimate prediction uncertainties.

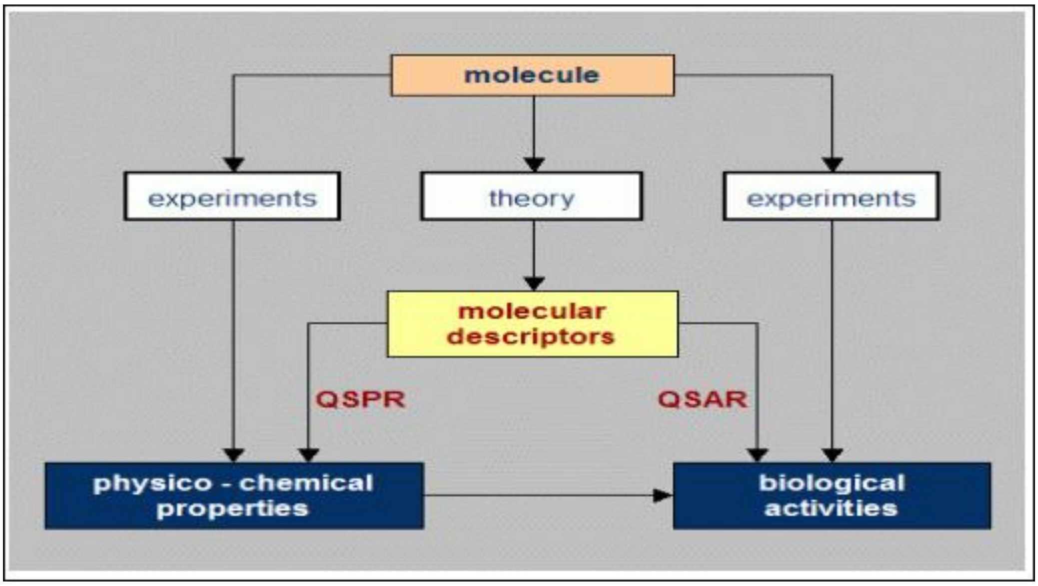

Figure III-1: *QSPRs / QSARs relative molecular structures with assessment criteria*

III. OPERATING PRINCIPALE

The principle of the QSPR/QSAR methods is to establish a mathematical relation quantitatively relating molecular properties, called descriptors, with a macroscopic observable (biological activity, toxicity, physico-chemical properties), for a series of similar chemical compounds using methods for the analysis of data. The general form of such a model is as follows:

Property / Activity = f (D 1 , D 2 ,... D n ,,, ...)
D 1 , D 2 , ...D n are descriptors of molecular structures.

The objective of such a method is to analyze structural data in order to detect determining factors for the property/activity measured. Once this relationship is established and validated, it can then be used for the Prediction of the property/activity of new molecules, for which the experimental values are not available. Such models can also be used to better understand the mechanisms and methods of activity practically speaking, the actual development of a model begins with collecting reliable experimental data in as large numbers as possible. The next step is to develop a series of descriptors that characterize molecular structures electronic and geometrical data of the compounds in the database in order to link them to the experimental property. Data analysis tools are then used to help to choose the appropriate descriptors and implement the model itself.

Once developed, the model must then be validated in terms of correlation (on the set of training data). Its robustness, which means the influence of the compounds of the set training on the model, is estimated by internal validation methods.

To estimate its predictive power, it is then necessary to have data available to determine the ability of the model to predict these values. Finally, for any model, it is important to know for which type of molecules it is usable or not and know its field of application.[4]

IV. MOLECULAR DESCRIPTORS: [3]

Descriptors are defined as the quantities that allows us to make maximum use of the information contained in the molecular structures, which are translated into a series of quantities (usually scalar) that quantify their physico-chemical and structural characteristics.

For decades, a great deal of work has been carried out to develop descriptors capable of describing molecular structures as exhaustively as possible. Today there are thousands of them, they can be calculated or empirical. Since the latter need to be measured, the descriptors calculated will be privileged.

A descriptor can also be defined as a numerical parameter specific to a particular chemical structure, also it is a result of a mathematical process or a certain experience standardized. These descriptors represent a means of correlating a chemical structure and a physico-chemical or biological property value. The descriptors are finally numerical intermediates replacing the molecule itself. These descriptors can be used to evaluate the influence of the molecular structure or the structure-properties, also for symmetry analysis and projection of the molecules

IV. 1. The importance of descriptors

- They indicate the description of the configuration (constitutional, topological, geometrical, electrostatic) of the molecule to be studied.
- It describes all the descriptive parameters of the molecule.

IV. 2. The choice of descriptors

In order to have the right choice of molecular descriptors we must respect the following points:

1. Descriptors must have a direct relationship, and a sufficient description for the molecular structure of the chemical compounds to be studied.
2. The descriptors must be related to the chemical properties and the activity of chemical compounds.
3. The simplicity of the descriptors.
4. The descriptive representation of the totality of the molecular structure of the composed.
5. The diversity of these descriptors.
6. The exact selection and distinction between the decisive (main) descriptors, and (secondary) deviations.
7. The simplicity and effectiveness of these descriptors, since the complexity causes a perturbation on the estimation result.
8. It is not necessary to have perfect relations, between the predictive variables (descriptors) because they cause regression difficulties.

V. THE USE OF QSPR MODELING IN DSSCs: [5]

Organic metal-free dyes are the most attractive sensitizers and they have known fast development over the last two decades, and this is because of their high extinction coefficients, nontoxicity properties, low coast and easy fabrication. Among all organic dyes that have been experimented, a specific range of organic dyes, which possess high energy conversion efficiency of more than 10.3%, have attracted significant attention as a new topic of research in order to obtain higher efficiencies.

The performance of a DSSC can be identified by evaluating some important factors, such as the power conversion efficiency (PCE), the photocurrent density measured at short-circuit (JSC), the open circuit voltage (VOC), the fill factor (FF), and the intensity of the incident light (Pin). The functional relationship linking these parameters is the following:

$$PCE = \frac{\mathrm{Jsc} \times \mathrm{Vco} \times \mathrm{FF}}{\mathrm{Pin}} \quad (1)$$

The PCE reflects the overall performance of the solar cell. However, the measurement of the photovoltaic parameters that affect the PCE can be complicated, and requires more accuracy. Therefore, a proper computational method for predicting the PCE is now used in the design of new sensitizers.

The use of quantum chemical calculations for molecular design of organic dyes is actually leading to great achievements. Using both of quantum chemical methods and machine learning methods is suitable to take full advantages from both methods. Quantum chemical methods can capture the physical essence of molecular systems, and machine learning methods can explore the central relationship between molecular structures and the target properties or observed activities through the quantum chemical molecular descriptors. As a result, researchers are applying quantum chemical methods with machine learning methods to investigate the quantitative structure–activity/property relationship (QSPR) of organic dyes in DSSCs that use a semiconductor TiO^2 film and a liquid electrolyte. With the QSPR model, the PCE of new organic dye sensitizers can be predicted, which cannot only save numerous resources but also provide some guidance for the synthesis of highly efficient dye sensitizers.

V. 1. Methods and materials: [6]

- **Dataset:**

The dataset should include the organic dyes as sensitizers with a TiO_2 film and a liquid electrolyte with experimental PCE values collected from literature. This dataset can cover all dyes available in the literature with taking in considerations the experimental conditions.

Generally, in dataset, dyes are divided into groups according to their molecular structure families (Arylamine dyes, indoline dyes, phenothiazine dyes…).

- **Structure Preparation, Molecular and Quantum Chemical Calculations (DFT/TD-DFT):**

The structure preparation is about the molecular geometries of dyes structures and their optimization. First of all, the structures should be drawn using Gauss view 5.0, then optimized considering particular molecular mechanics method. Geometry optimizations are performed using the Density Functional Theory (DFT and TD-DFT) methods implemented in GAUSSIAN 09 software. Those methods are selected with great care to give reasonable prediction for the excitation energies and the absorption spectra of molecules.

- **Descriptor Selection:**

Descriptor selection is based on exploring the Gaussian output files from the DFT/TD-DFT and computed basic quantum mechanical descriptors for computation of the different constitutional groups from the optimized structures to identify the most important fragments that are important for better PCE. All the quantities related to DFT/TD-DFT properties are extracted for building QSPR models.

Choosing the right descriptor requires knowing important parameters such as the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the valence band, the conduction band. Also, the properties from the DFT study that includes absorption spectrum and the ability to interact with the semiconductor oxide surface which have a direct effect on the PCE, must be considered.

Concerning the descriptors that indicate the stability of the molecules and the electron’s transition properties, they can be provided by the TD-DFT calculations.

- **Data Pre-Processing and Splitting:**

In this phase, the descriptors are pretreated to eliminate the correlation and reduce the noise level between them. Then, an algorithm is applied to select the best possible set of descriptors for the QSPR modeling. The identified ones should be the best that reflects the properties of the studied dyes. In order to obtain the most significant QSPR model, a selection of training and test sets is highly recommended.

- **Model Development and Validation:**

The QSPR mode is developed using the training set compounds from the algorithm used, following by multiple linear regression analysis.

- **Model Validation and Metrics and Y-Randomization:**

In order to verify the model, different internal and external methodologies are employed. The equation that represents the QSPR is judged using the determination coefficient R^2

Concerning Y randomization, it is used also as a tool to validate the QSPR model. It is based on the comparison between the original model in data descriptor and models built for randomly permuted response.

- **Applicability Domain Study:**

An acceptable QSPR model should possess a defined AD (applicability domain), which represents the chemical space defined by the structural information extracted from the chemicals used in model development.

The key aspects in defining the AD of QSPR model are the following:

- Identification of the subspace of chemical structures that can be predicted reliably.
- Defined AD determines the degree of generalization of a given predictive model. Thus, if the AD is too restricted, it implies the model can provide reliable predictions for very limited chemical categories.
- A well-defined AD indicates if the endpoint for the chemical structures under evaluation can be reliably predicted.
- Characterization of the interpolation space is very significant to define the AD for a given QSPR model.

VI. QUANTUM CHEMICAL USED FOR QSPR MODELING IN DSSCs:

The development of QSPR/QSAR models is based on the calculation of descriptors, which are ensured through the use of the molecular structures modeling. Different approaches can be envisaged in the framework of modelling tool, in our case which is the Gauss view 5.0 and Gaussian 09 softwares. Quantum methods are the most important methods, not only for the descriptors calculation, but also necessary for the development of predictive models, the theory of density functional and semi-empirical methods are capable of calculating several system properties. It is for this reason that these approaches have been used in our study.

An accurate description of systems requires quantum mechanics, which are mostly based on Schrödinger equation.

VI. 1. Schrödinger equation:

The solution to the Schrödinger equation gives a wave function Ψ. All physical properties of the system can then be extracted from this wave-function. The time-dependent Schrödinger equation for a particle described by the wave function Ψ and moving in a potential V is a linear differential (2nd order partial differential) equation:

$$\boxed{i\hbar \frac{\partial \Psi(r,t)}{\partial t} == \frac{-\hbar^2}{2\text{m}} \nabla^2 \Psi(r,t) + V\Psi(r,t)}$$

Where Ψ is the wave function, r the position and t time. ∇^2 is the Laplace operator, V the Potential energy operator and ħ is the Planck's constant divided by 2π. The Hamiltonian operator is defined as:

$$\boxed{H = \left[\frac{-\hbar^2}{2\text{m}} \nabla^2 + V\right]}$$

VI. 2. Density functional theory:

Instead of using the wave function with spin and spatial coordinates for every single electron, another theory can be considered. The Density Functional Theory (DFT) is a computationally efficient way of including electron correlation. The system is described by an electron density, rather than a sum of independent electrons, and the Hamiltonian is then only dependent on position and atomic number of the nuclei and the total number of electrons. The governing equation is still the electronic Schrödinger equation but the total energy of the system is expressed as a function of the electron density ρ(r):

$$\boxed{E[\rho(r)] = T[\rho(r)] + E_{ne}[\rho(r)] + E_{ee}[\rho(r)]}$$

VI. 3. The time-dependent DFT (TD-DFT)

The time-dependent DFT (TD-DFT) is an extension of DFT that handles electronic excited states. Physical properties such as absorption spectra can easily be calculated. For the extraction of the excited states, the system is simply subjected to an external time-dependent electric field that is treated as a small perturbation within a linear response theory. The perturbation can for instance be atomic motions or light. Excitation energies can then be calculated without computing all the excited-state wave functions, they are simply determined by poles of the response function. In a variational form, each excitation energy and associated oscillator strength (transition probability) can then be calculated iteratively. TD-DFT gives a good first estimation of physical processes such as photoexcitation, for which information about the excited states is wanted. However, since the virtual orbitals in general are quite poor, this method should be handled with care and only be used for the lowest excitations.

VII. CONCLUSION

The QSPR model allows the identification of essential fragments and structural features of organic dyes that are most responsible for the high PCE of DSSCs explicit to liquid electrolytes through a stringent validation approach.

The QSPR model enables identification of the essential structural that are necessary for quantifying the prime molecular properties of diverse organic dyes systems that could guide the design and synthesis of more efficient dyes in the near future. The interpretation of the model could reveal that a higher number of substitutions from the studied family of dyes that enable rapid electron injection into the semiconductor. This dynamic step allows efficient regeneration of the oxidized dye and helps to achieve a higher PCE value for dye-sensitized solar cell explicit to liquid electrolytes.

The QSPR model, developed for diverse organic dyes, is an efficient tool to screen a wide range of dyes, allowing the identification of dyes with high PCE in a time- and cost-effective manner.

The developed QSPR model will enable scientists to reduce their experimental effort, time, and resources. In addition, the exploratory features may assist in designing more efficient units for DSSCs.

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Chapter IV : RESULTS AND DISCUSSION

I. INTRODUCTION

As known, the organic dye is the most important component in DSSCs, it plays an important role in determining cell performance. However, it should satisfy these essential characteristics:

- A good absorption of solar light.
- The dye should have at least one anchoring group (COOH,PO3H2…) to bind strongly the dye to the semiconductor surface.
- The LUMO energy of the dye should be higher than the conduction band edge of the semiconductor so that electrons can be transferred efficiently from the excited dye to the conduction band of TiO_2. Moreover, the HOMO energy of the dye should be lower than the energy level of the electrolyte for the dye regeneration.
- Unfavorable dye aggregation on the semiconductor surface should be avoided through optimization of the molecular structure of the dye or by addition of coadsorbers that prevent aggregation. However, controlled dye aggregates can lead to an improved performance compared with a monomer dye layer.
- The dye should be photostable, thermally stable, and electrochemically stable. [1]

To this end, to study intensively the properties of the dye in order to improve the power conversion efficiency for DSSCs, Quantitative Structure-Property Relationship (QSPR) models are now increasingly used, due to the growth in computing tools. These models used for the prediction of properties of untested chemicals are also used for prioritization of synthesis and experimental testing of new compounds. In addition, the validation of QSPR models plays a crucial role in judging the reliability of their predictions.

In this chapter, we established the final predictive model and its effectiveness has been tested.

II. METHODS AND MATERIALS USED

We used the molecular modeling tools "QSPR" and "Molecular Docking" of the MOE software (Molecular Operating Environment, version of 2015).

The datasets that we used in our manuscript were established from the work of A.F Buene et all.[2]

We reviewed the structures and collected the necessary information from the literature in order to use it in the preparation of our datasets, also to get good results and a strong valid model, we selected a group of structures in which, all observed parameters were available.

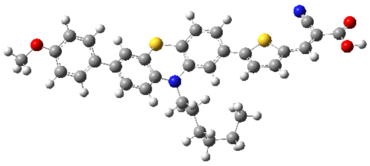
III. DFT RESULTS

III. 1. Geometry optimization

All of the geometries and properties of the molecules in the datasets were calculated by DFT methods using the GAUSSIAN09 software. The calculations in this study were performed using the B3LYP method with basis sets 6–31G*.

To simplify the model and improve its practicability, we intend to use descriptors generated from both quantum chemical calculations and direct counts of structures. On the basis of the operational principles of DSSCs, some properties of dye sensitizers are significantly affecting the PCE, such as absorption spectrum, ability of interacting with semiconductor oxide surface, excitation energy level, and the stability. In DFT calculations, all the quantities related to these properties are extracted to build the QSPR model.

The structures are presented in the following figure:



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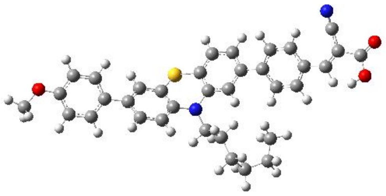

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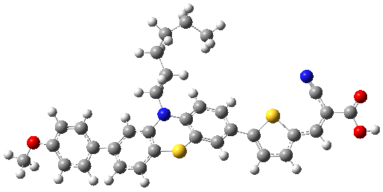

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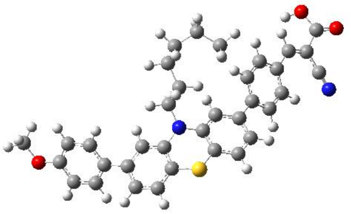
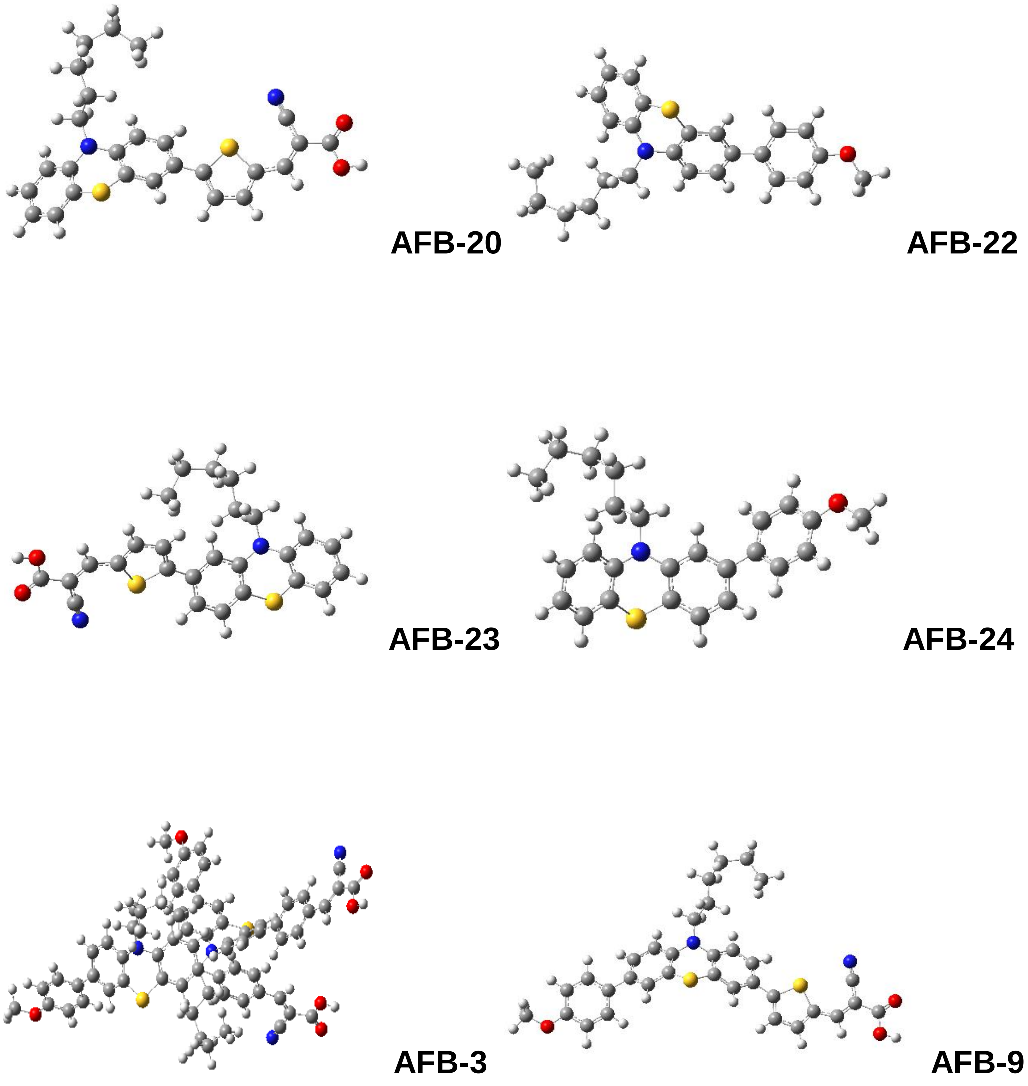


AFB-28



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AFB-23 AFB-24

AFB-3 AFB-9

Figure IV-1:*Molecular structures of sensitizers used in this study.*

III. 2. Electronic parameters

In addition to the electronic structure, the electronic parameters of DSSCs can be calculated using both density functional theory and time-dependent TD-DFT. also the critical parameters that govern the values of the vital characteristics of solar cells: short-circuit current and open circuit voltage. All critical parameters, including light absorption spectra, electron injection, charge recombination, conduction band edge (CB) displacement, as well as excited state lifetime of the electron and photostability of the dye can be calculated.

III. 3. II.3. HOMO/LUMO energies

- The HOMO energy :(EHOMO)
  Highest Occupied Molecular Orbital is the highest energy level in the molecule that contains electrons, it is directly related to the ionization potential and compared to the top of the valence band in inorganic semiconductors.
- The LUMO energy:(ELUMO)
  Lowest Unoccupied Molecular Orbital is the lowest energy level in the molecule that does not contain electrons, it is directly related to electron affinity.

They play a major role in many chemical reactions and reaction mechanisms. The energies of these orbitals are very popular parameters in quantum chemistry and QSAR studies. These energies have been calculated and extracted from standard Gaussian output files.

The electron populations of the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) were calculated to show the electron population locations and the energy of the molecular orbit.

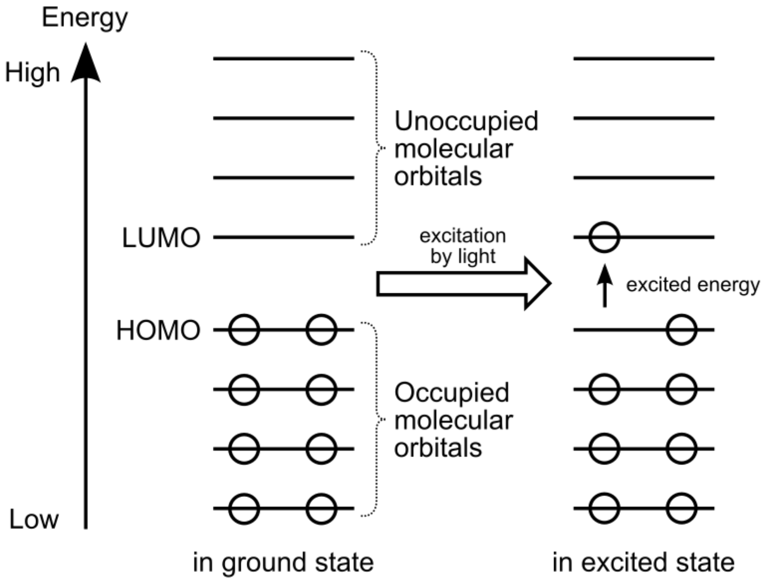
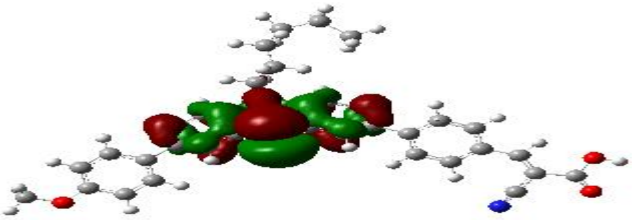
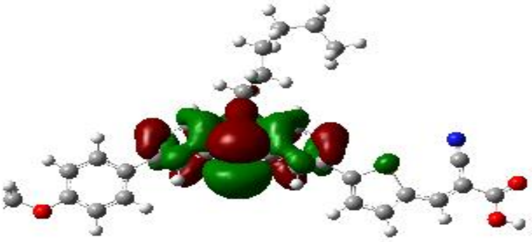
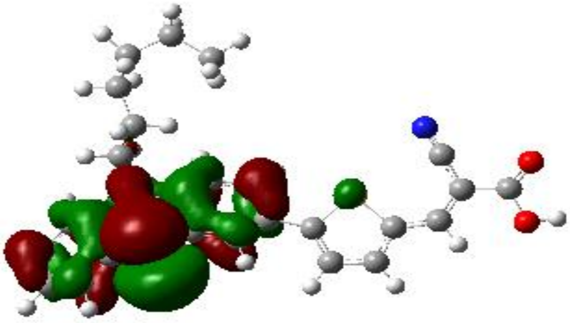
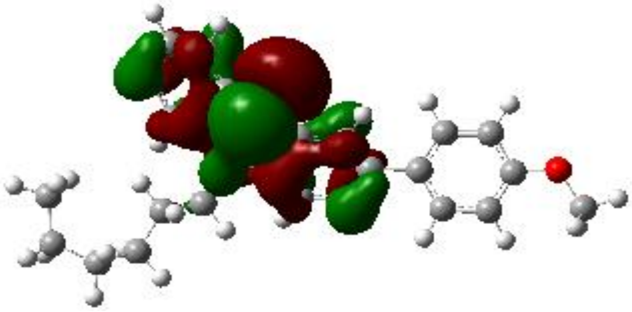
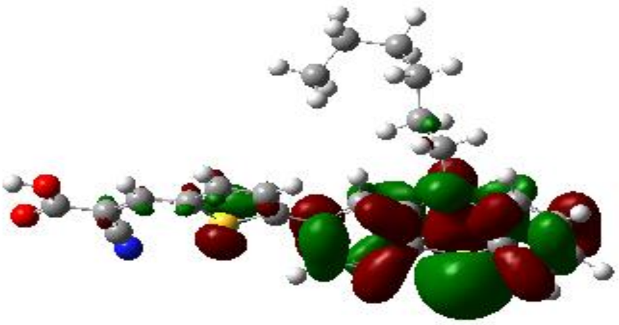
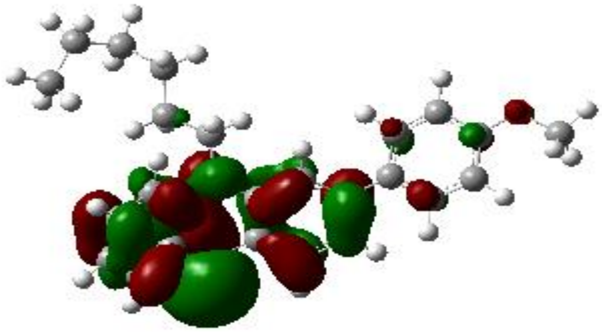
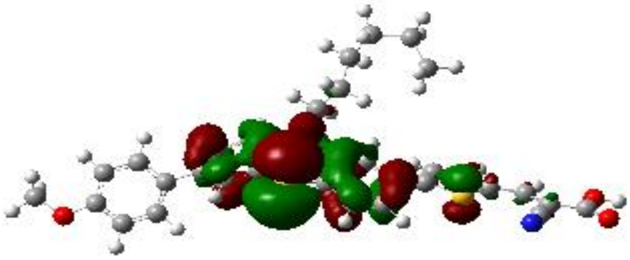
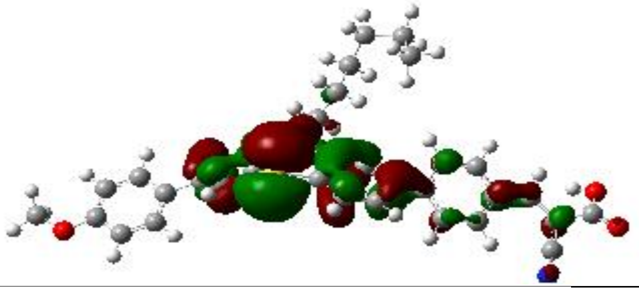
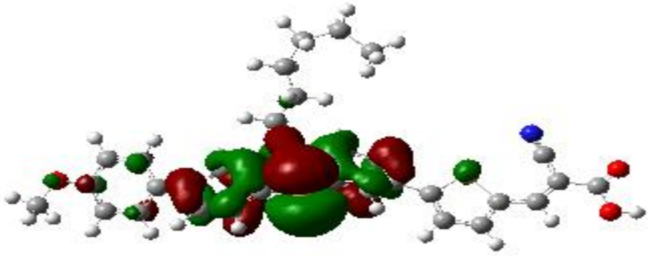
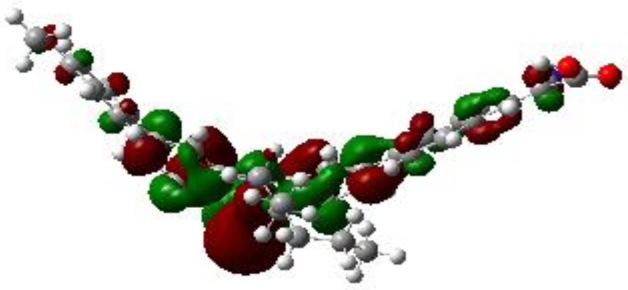


Figure IV-2*:Diagram of the HOMO and LUMO of a molecule. Each circle represents an electron in an orbital; when light of a high enough frequency is absorbed by an electron in the HOMO, it jumps to the LUMO.*

Table IV-1*: HOMO energy and electron distribution.*

Dye	HOMO energy (au)	Electron distribution in HOMO level

AFB-3	-0.2626	
AFB-9	-0.2617	
AFB-20	-0.2923	
AFB-22	-0.2633	
AFB-23	-.02621	

AFB-24	-0.2631	
AFB-25	-0.2615	
AFB-26	-0.2616	
AFB-27	-0.2639	
AFB-28	-0.2637	

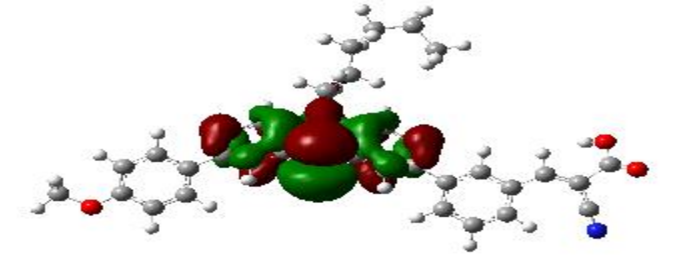
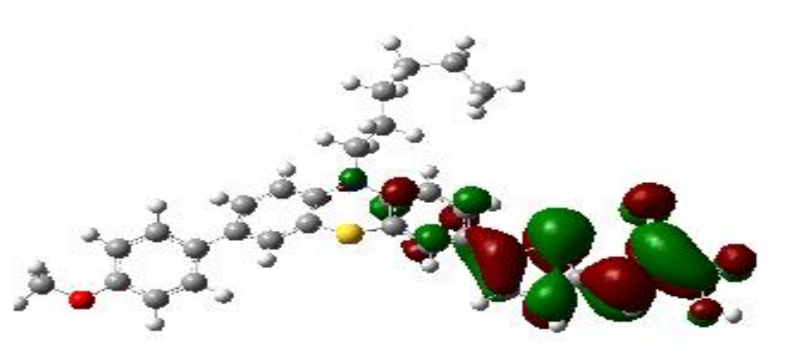
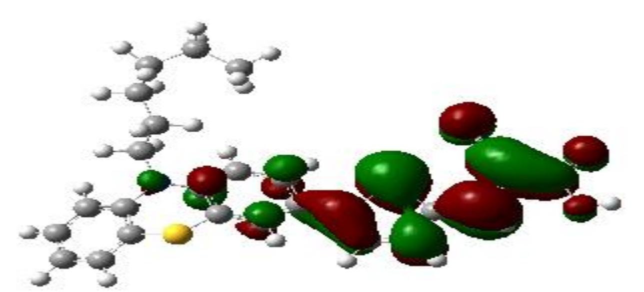
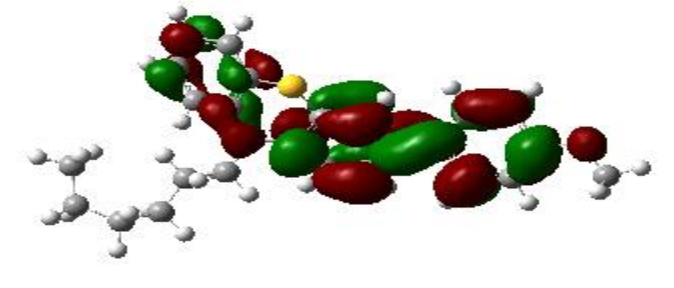
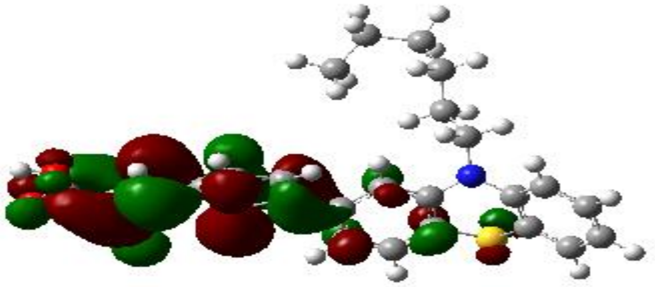
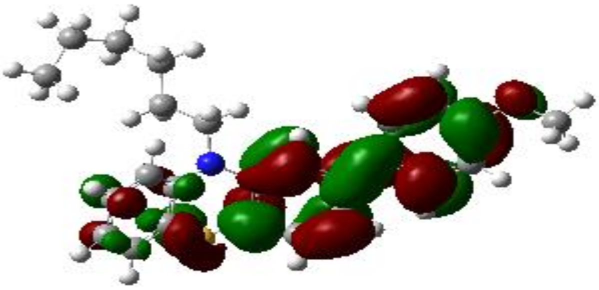
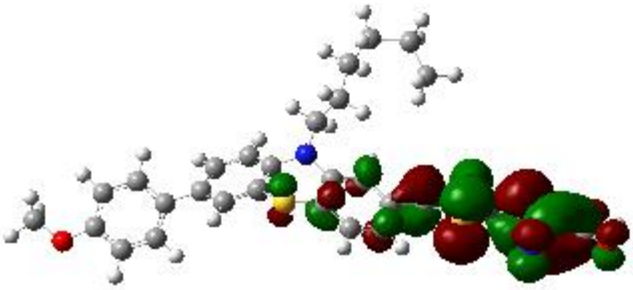
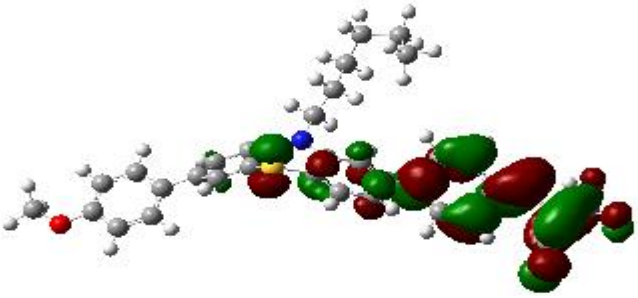
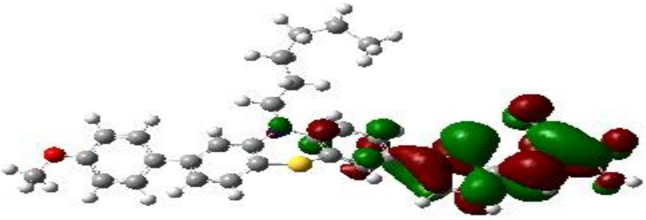
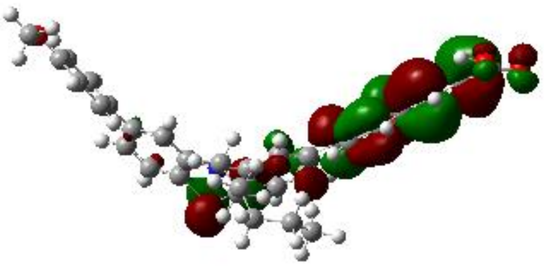
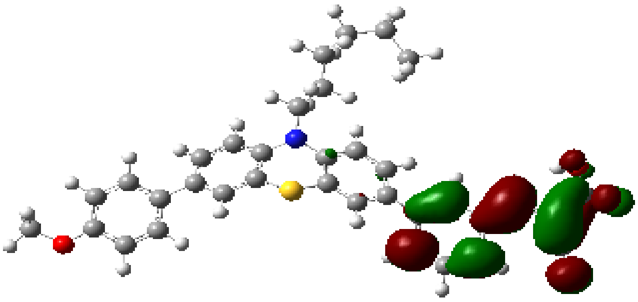
AFB-29	-0.2627	

Table IV-2: LUMO energy and electron distribution.

Dye	Electron distribution in LUMO level	LUMO energy (au)
AFB-3		-0.2372
AFB-9		-0.2204
AFB-20		-0.2204
AFB-22		-0.1848

AFB-23		-0.2199
AFB-24		-0.1843
AFB-25		-0.2199
AFB-26		-0.2204
AFB-27		-0.2343

AFB-28		-0.2343
AFB-29		-0.2333

As shown in the two previous tables, HOMO and LUMO energy levels of our studied dyes represent good values as sensitizers for DSSCs, it means they have an important ability to absorb a wide range of the visible light which leads to an efficient electron injection from the valence band to the conduction band of the semiconductor (TiO_2).

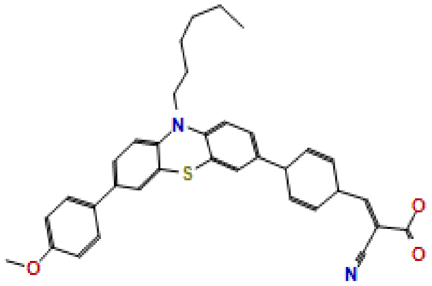
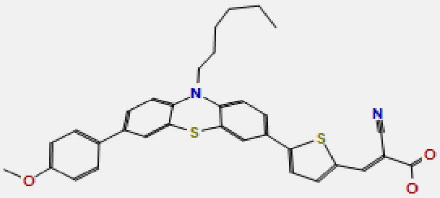
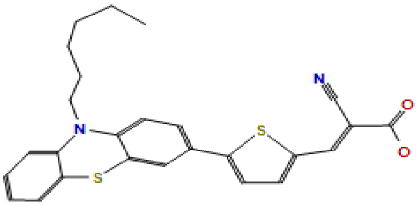
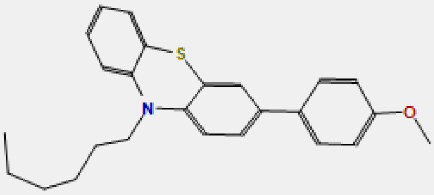
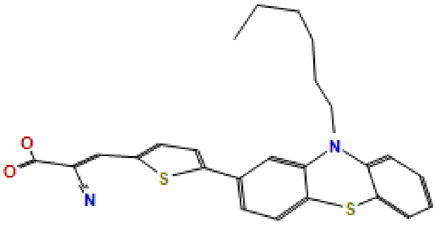
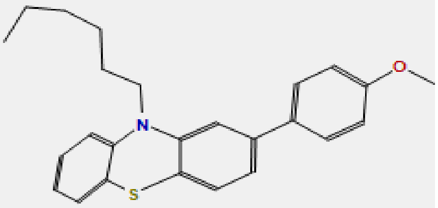
IV. THE QSPR MODEL

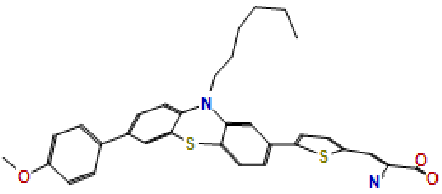
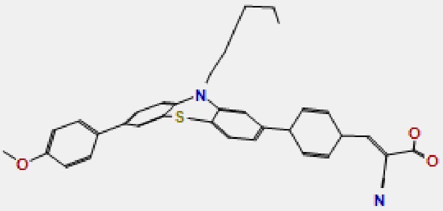
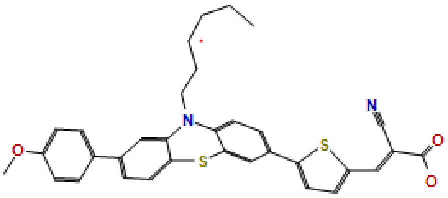
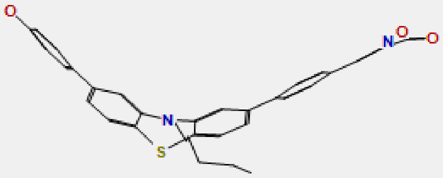
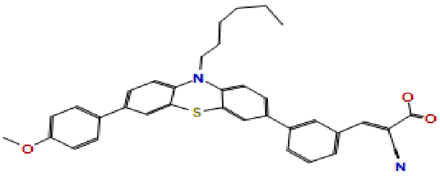
IV. 1. Dataset

The selection of the experimental learning data set is a crucial step in any QSPR analysis. Our data set covers 11 different possible phenothiazines (C12H9NS) available in literature taking into consideration the experimental power conversion efficiency values. Therefore, although the dataset isn't that large, it is still the only one available.

The chemical structures and experimental PCE values for all compounds are given in Table3.

Table IV-3: Chemical structures of the organic sensitizers with their experimental efficiency values (PCE).

Components	Molecular structure	Efficiency (%) PCE
AFB-3		4.37 %
AFB-9		5.82 %
AFB-20		5.34 %
AFB-22		4.06 %
AFB-23		3.48 %
AFB-24		2.27 %

AFB-25		4.27 %
AFB-26		3.43 %
AFB-27		5.78 %
AFB-28		4.67 %
AFB-29		1.06 %

IV. 2. Calculation steps and details

First of all, the geometries of our sensitizers have been optimized by density functional theory methods (FDT) using the exchange-correlation function of B3LYP with 6-31G(d) basis sets of GaussView 05 software and then, electronic properties needed are obtained.

In this work, six QSPR models have been developed using the experimental PCE data. Calculations were first started using a total of 124 different i3D descriptors exploited in the MOE software, these sets of descriptors were first pre-processed with a variance threshold of 0.0001 and passed through a correlation coefficient of 0.99 in order to eliminate correlations between noise level and the input descriptors. Next, a genetic algorithm (GA) was applied to select the best possible set of descriptors for QSPR modelling from the pre-processed pool of descriptors. This "descriptor elucidation" procedure allowed us to select six most significant descriptors to build our QSPR model which are: **BCUT_SLOGP2, b_1rotR, b_rotR, MNDO_LUMO, PM3_LUMO, Vsurf_DW.** Therefore, the descriptors identified are the most relevant for our study as they may reflect the required properties of all the studied dyes.

IV. 3. Descriptor's analysis

❖ Correlation coefficient

For all descriptors used, the calculation of the linear correlation coefficient R between each pair of the set of descriptors is greater or equal to 0.5 ($R \geq 0.5$), except for the first model.

The stability and robustness of the models developed are then evaluated using correlation coefficients (R^2), standard deviations and Fisher F criteria. In addition, the choice of descriptors was supported by a Student test at a 95% confidence level. All models were cross-validated using a Leave-One Out (LOO) procedure. In some cases, other partition types (Leave-Many-Out) were also used. By convention, and without any indication to the contrary, the R^2cvs presented are the result of a LOO procedure. Whenever possible (sufficient number of molecules), the model was evaluated by external validation from data not included in the training set. The predictive power is then characterized by the correlation coefficient for this validation set (R^2 ext).

Table IV-4*; descriptors signification*

Descriptors	**Signification**
BCUT_SLOGP2	BCUT descriptors using atomic contribution to logP (using the Wildman and Crippen SlogP method) instead of partial charge.
b_1rotR	Fraction of rotatable single bonds: b_1rotN divided by b_heavy.
b_rotR	Fraction of rotatable bonds: b_rotN divided by b_heavy
MNDO_LUMO	The energy (eV) of the Lowest Unoccupied Molecular Orbital calculated using the MNDO Hamiltonian [MOPAC].
PM3_LUMO	The energy (eV) of the Lowest Unoccupied Molecular Orbital calculated using the PM3 Hamiltonian [MOPAC].
Vsurf_DW13	Contact distances of vsurf_EWmin (3 descriptors)

***Table IV-5**: Correlation coefficient values of selected descriptors.*

Descrtiptor	R^2 value
BCUT_SLOGP_2	0.23518
b_1rotR	0.27894
b_rotR	0.27894
MNDO_LUMO	0.24780
PM3_LUMO	0.24711
vsurf_DW13	0.63899

IV. 4. QSPR selected models:

The models established are in the following table:

Molecule	PCE %	Descriptors			Model 1					
		BCUT_SLOGP_2	b_rotR	vsurf_DW13	$PRED	$RES	$Z-SCORE	$XPRED	$XRES	$XZ-SCORE
1	4.37	0.7652	0.2444	0.5	4.1522	0.2177	0.34846	4.0405	0.3294	0.5068
2	5.82	0.8059	0.25	0.5	4.9873	0.8326	1.3323	4.8398	0.9801	1.6614
3	5.34	0.8480	0.2571	0.5	5.7969	-0.4569	0.7312	6.0776	-0.7376	1.1723
4	4.06	0.8557	0.2571	0.7071	4.5019	-0.4419	0.70711	4.9621	-0.9021	1.4450
5	3.48	0.7732	0.2258	0.7071	3.6177	-0.1377	0.2203	3.7581	-0.2781	0.4262
6	2.27	0.7923	0.2258	1	2.0020	0.2679	0.4287	1.4686	0.8013	1.2543
7	4.27	0.8059	0.25	0.7071	3.4939	0.7760	1.2418	3.3065	0.9634	1.6173
8	3.43	0.7823	0.2444	0.5	4.5979	-1.1679	1.8688	4.8924	-1.4624	2.8746
9	5.87	0.8059	0.25	0.5	4.9873	0.8826	1.4123	4.8310	1.0389	1.7873
10	4.67	0.79648	0.2444	0.5	4.9654	-0.2954	0.4727	5.0312	-0.3612	0.5580
11	1.06	0.7661	0.2444	0.8660	1.5371	-0.4771	0.7635	2.7713	-1.7113	2.9012

Table IV-6: model 1.

Table IV-7: Model 2.

Molecule	PCE %	Descriptors			Model 2					
		b_1rotR	b_rotR	vsurf_DW13	$PRED	$RES	$Z-SCORE	$XPRED	$XRES	$XZ-SCORE
1	4.3700	0.2222	0.2444	0.5000	4.0955	0.2745	0.6552	3.9856	0.3844	0.8996
2	5.8200	0.2273	0.2500	0.5000	5.5372	0.2828	0.6749	5.4627	0.3573	0.8352
3	5.3400	0.2286	0.2571	0.5000	5.7866	-0.4466	1.0659	5.9904	-0.6504	1.6057
4	4.0600	0.2286	0.2571	0.7071	4.2378	-0.1778	0.4244	4.3589	-0.2989	0.6897
5	3.4800	0.2258	0.2258	0.7071	4.0492	-0.5692	1.3583	4.8244	-1.3444	3.9369
6	2.2700	0.2258	0.2258	1.0000	1.8589	0.4111	0.9812	1.2172	1.0528	2.7195
7	4.2700	0.2273	0.2500	0.7071	3.9884	0.2816	0.6720	3.9220	0.3480	0.8129
8	3.4300	0.2222	0.2444	0.5000	4.0955	-0.6655	1.5882	4.3618	-0.9318	2.5732
9	5.8700	0.2273	0.2500	0.5000	5.5372	0.3328	0.7942	5.4495	0.4205	0.9934
10	4.6700	0.2222	0.2444	0.5000	4.0955	0.5745	1.3711	3.8655	0.8045	2.0987
11	1.0600	0.2222	0.2444	0.8660	1.3583	-0.2983	0.7118	1.8663	-0.8063	1.9608

***Table IV-8**: Model 3*

Molecule	PCE %	Descriptors			Model 3					
		b_1rotR	MNDO_LUMO	vsurf_DW13	$PRED	$RES	$Z-SCORE	$XPRED	$XRES	$XZ-SCORE
1	4.3700	0.2222	-0.6111	0.5000	4.2210	0.1490	0.3584	4.1439	0.2261	0.5233
2	5.8200	0.2273	-1.0204	0.5000	5.5278	0.2922	0.7031	5.4522	0.3678	0.8688
3	5.3400	0.2286	-1.2175	0.5000	5.8064	-0.4664	1.1221	6.0103	-0.6703	1.6825
4	4.0600	0.2286	-1.2135	0.7071	4.2640	-0.2040	0.4908	4.3769	-0.3169	0.7396
5	3.4800	0.2258	-0.1874	0.7071	4.0508	-0.5708	1.3733	4.7059	-1.2259	3.5383
6	2.2700	0.2258	-0.1818	1.0000	1.8695	0.4005	0.9637	1.2386	1.0314	2.6746
7	4.2700	0.2273	-0.9612	0.7071	4.0200	0.2500	0.6015	3.9687	0.3013	0.7053
8	3.4300	0.2222	-0.8828	0.5000	4.0509	-0.6209	1.4939	4.3044	-0.8744	2.3736
9	5.8700	0.2273	-1.1468	0.5000	5.4487	0.4213	1.0137	5.3375	0.5325	1.3009
10	4.6700	0.2222	-0.8510	0.5000	4.0708	0.5992	1.4418	3.8301	0.8399	2.2473
11	1.0600	0.2222	-0.8992	0.8660	1.3102	-0.2502	0.6021	1.8701	-0.8101	1.9662

Table IV-9: *Model 4.*

Molecule	PCE %	Descriptors			Model 4					
		BCUT_SLOGP_2	MNDO_LUMO	vsurf_DW13	$PRED	$RES	$Z-SCORE	$XPRED	$XRES	$XZ-SCORE
1	4.3700	0.7652	-0.6111	0.5000	4.3813	-0.0113	0.0181	4.3870	-0.0170	0.0260
2	5.8200	0.8059	-1.0204	0.5000	4.9697	0.8503	1.3590	4.8179	1.0021	1.7051
3	5.3400	0.8481	-1.2175	0.5000	5.8275	-0.4875	0.7791	6.1343	-0.7943	1.2688
4	4.0600	0.8557	-1.2135	0.7071	4.5574	-0.4974	0.7949	5.0480	-0.9880	1.5996
5	3.4800	0.7733	-0.1874	0.7071	3.5806	-0.1006	0.1607	3.6660	-0.1860	0.2841
6	2.2700	0.7924	-0.1818	1.0000	1.9955	0.2745	0.4388	1.4585	0.8115	1.2700
7	4.2700	0.8059	-0.9612	0.7071	3.5659	0.7041	1.1254	3.4382	0.8318	1.3636
8	3.4300	0.7824	-0.8828	0.5000	4.5206	-1.0906	1.7431	4.8032	-1.3732	2.5912
9	5.8700	0.8059	-1.1468	0.5000	4.8317	1.0383	1.6595	4.5856	1.2844	2.3558
10	4.6700	0.7965	-0.8510	0.5000	4.9148	-0.2449	0.3913	4.9636	-0.2936	0.4511
11	1.0600	0.7661	-0.8992	0.8660	1.4951	-0.4351	0.6954	3.1605	-2.1005	3.6064

***Table IV-10**: Model 5.*

Molecule	PCE %	Descriptors			Model 5					
		BCUT_SLOGP_2	b_1rotR	vsurf_DW13	$PRED	$RES	$Z-SCORE	$XPRED	$XRES	$XZ-SCORE
1	4.3700	0.7652	0.2222	0.5000	4.1645	0.2055	0.4753	4.0672	0.3028	0.6782
2	5.8200	0.8059	0.2273	0.5000	5.6044	0.2156	0.4987	5.5222	0.2978	0.6673
3	5.3400	0.8481	0.2286	0.5000	5.7416	-0.4016	0.9290	5.9848	-0.6448	1.5211
4	4.0600	0.8557	0.2286	0.7071	4.2326	-0.1726	0.3993	4.4365	-0.3765	0.8438
5	3.4800	0.7733	0.2258	0.7071	3.8865	-0.4065	0.9401	4.1196	-0.6396	1.5092
6	2.2700	0.7924	0.2258	1.0000	1.6914	0.5786	1.3383	1.0674	1.2026	3.2608
7	4.2700	0.8059	0.2273	0.7071	4.1515	0.1185	0.2742	4.1260	0.1440	0.3190
8	3.4300	0.7824	0.2222	0.5000	4.0386	-0.6086	1.4077	4.3002	-0.8702	2.2272
9	5.8700	0.8059	0.2273	0.5000	5.6044	0.2656	0.6143	5.5031	0.3669	0.8290
10	4.6700	0.7965	0.2222	0.5000	3.9347	0.7353	1.7007	3.3805	1.2895	3.8742
11	1.0600	0.7661	0.2222	0.8660	1.5898	-0.5298	1.2254	1.9684	-0.9084	2.2890

Table IV-11: *Model 6.*

Molecule	PCE %	Descriptors			Model 6					
		b_1rotR	PM3_LUMO	vsurf_DW13	$PRED	$RES	$Z-SCORE	$XPRED	$XRES	$XZ-SCORE
1	4.3700	0.2222	-1.2617	0.5000	4.1552	0.2148	0.4888	4.0481	0.3219	0.7103
2	5.8200	0.2273	-1.6939	0.5000	5.5064	0.3136	0.7138	5.4262	0.3938	0.8806
3	5.3400	0.2286	-1.8002	0.5000	5.8549	-0.5149	1.1719	6.0719	-0.7319	1.7512
4	4.0600	0.2286	-1.7704	0.7071	4.3739	-0.3139	0.7145	4.5147	-0.4547	1.0215
5	3.4800	0.2258	-0.3564	0.7071	3.8961	-0.4161	0.9471	4.4874	-1.0074	2.4401
6	2.2700	0.2258	-0.3895	1.0000	1.7849	0.4851	1.1040	1.0599	1.2102	3.0872
7	4.2700	0.2273	-1.8617	0.7071	3.9814	0.2886	0.6567	3.8694	0.4006	0.8941
8	3.4300	0.2222	-1.6001	0.5000	4.0800	-0.6500	1.4793	4.3407	-0.9107	2.3271
9	5.8700	0.2273	-1.8164	0.5000	5.4791	0.3909	0.8896	5.3785	0.4915	1.1183
10	4.6700	0.2222	-1.7117	0.5000	4.0551	0.6149	1.3994	3.7954	0.8746	2.1963
11	1.0600	0.2222	-1.5014	0.8660	1.4728	-0.4128	0.9395	2.1014	-1.0414	2.5304

IV. 5. Model evaluation

IV. 5. 1. . *Internal validation*

Table IV-12: *QSPR models equations and cross-validated coefficients.*

Model	Equation	RMSE (cv)	R^2 (cv)
1	PCE= -2.131455-(7.21093*vsurf_DW13)-(40.20253*b_rotR)+(26.00520*BCUT_SLOGP_2)	0.9701	0.54517
2	PCE= -55.60109+(308.81014 * b_1rotR)-(21.22701 * b_rotR)-(7.47817 * vsurf_DW13)	0.74876	0.73402
3	PCE= -60.44495 +(309.50289 * b_1rotR)+(0.62626 * MNDO_LUMO) -(7.45951 * vsurf_DW13)	0.72634	0.74546
4	PCE=-10.87321+(25.44033*BCUT_SLOGP_2)+(1.09216*MNDO_LUMO)-(7.09075* vsurf_DW13)	1.04578	0.47802
5	PCE= -63.21981 - (7.34896 * BCUT_SLOGP_2)+(344.32020 * b_1rotR -(7.01548 * vsurf_DW13)	0.73818	0.74295
6	PCE= -55.6537+(286.56470 * b_1rotR)+(0.22245 * PM3_LUMO) -(7.18287 * vsurf_DW13)	0.77232	0.71594

- **Explanations**

- Internal validation of QSPR models is based on two main parameters which are Square correlation coefficient R^2 and the Root mean square error RMSE.

- R^2 allows us to compare between the predicted and experimental studied properties, in our case, the power conversion efficiency PCE. A good model must have a value of R^2 above or equal to 0.5.

- RMSE is mostly used to decide if the QSPR model possesses the predictive quality reflected in R^2 , it shows us the error between the mean of the experimental values and the predicted properties. If RMSE is above 1 (RMSE >1), the model have a poor ability to predict the properties even with a good R^2 value.

- R^2 and RMSE parameters are not sufficient to judge the QSPR validity, that's why cross validation is required. Cross validation R^2cv is used to permit the determination of how large the model can be used for a random data set and also to evaluate the predictive power of the model's equation.

- ZSCORE and XZSCORE represent the standardized value that specifies the exact location of an X value within a distribution by describing its distance from the mean in terms of standard deviation units. This subset must be examined carefully to detect errors or to determine new descriptors to be calculated, in these models, we obtained values of both ZSCORE and XZSCORE less than 2.5, which means the models are good to be used.

- As shown in table 7, five from the six chosen QSPR models have a good value of R^2 cv and RMSEcv (R^2 cv >0.5 and RMSE <1), according to that, we can say that a good and valid model was established. Only the model number 4 is considered as a poor model (RMSE=1.04578, R^2cv=0.47802).

- The best model in our work is model number 3.

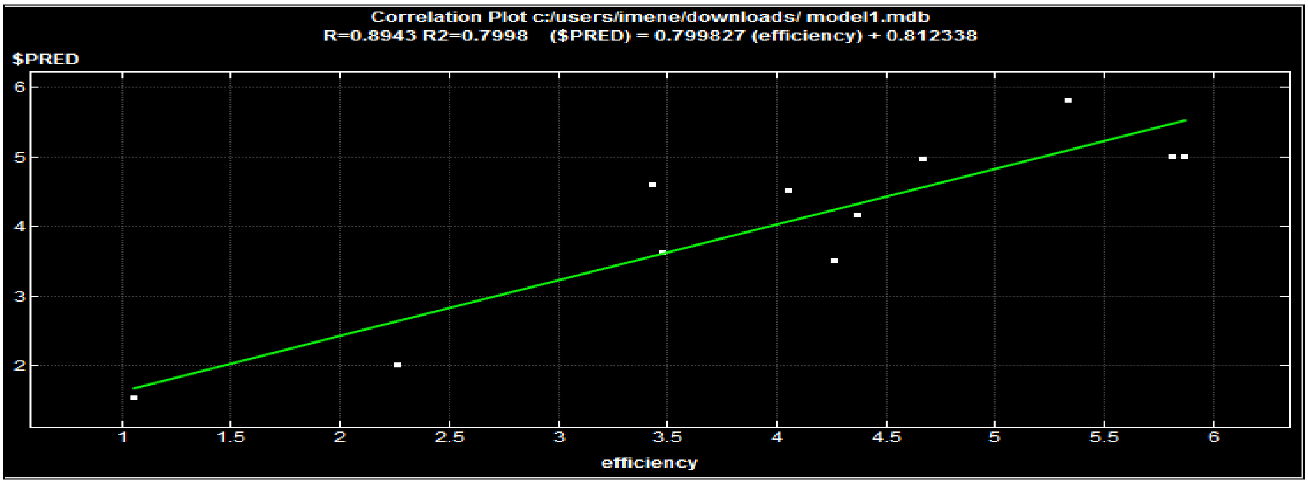


Figure IV-3: *correlation of model 1.*

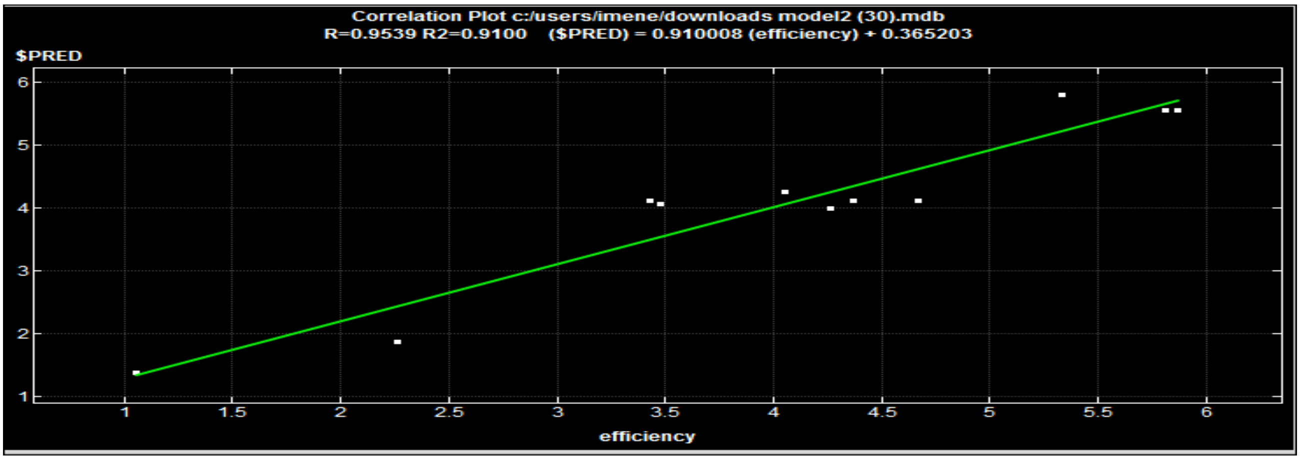


Figure IV-4: *correlation of model 2.*

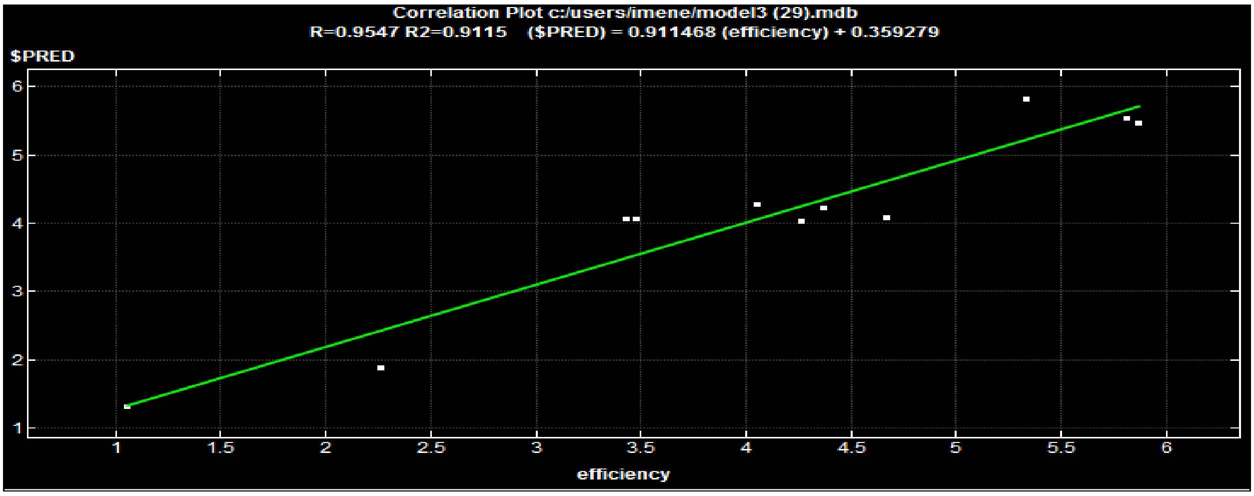


***Figure IV-5**: Correlation of model 3.*

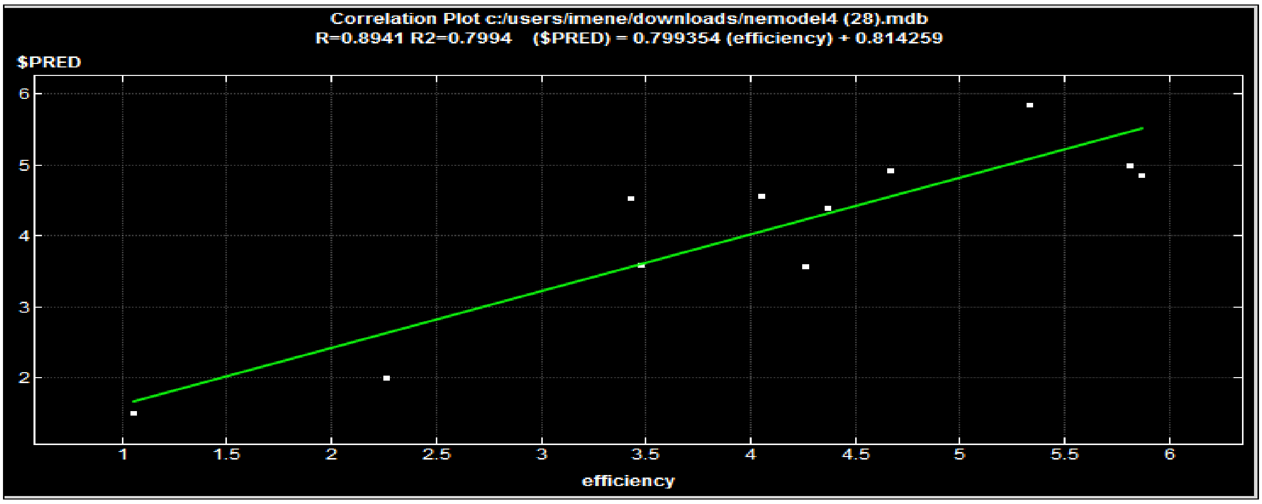


***Figure IV-6:** Correlation of model 4*

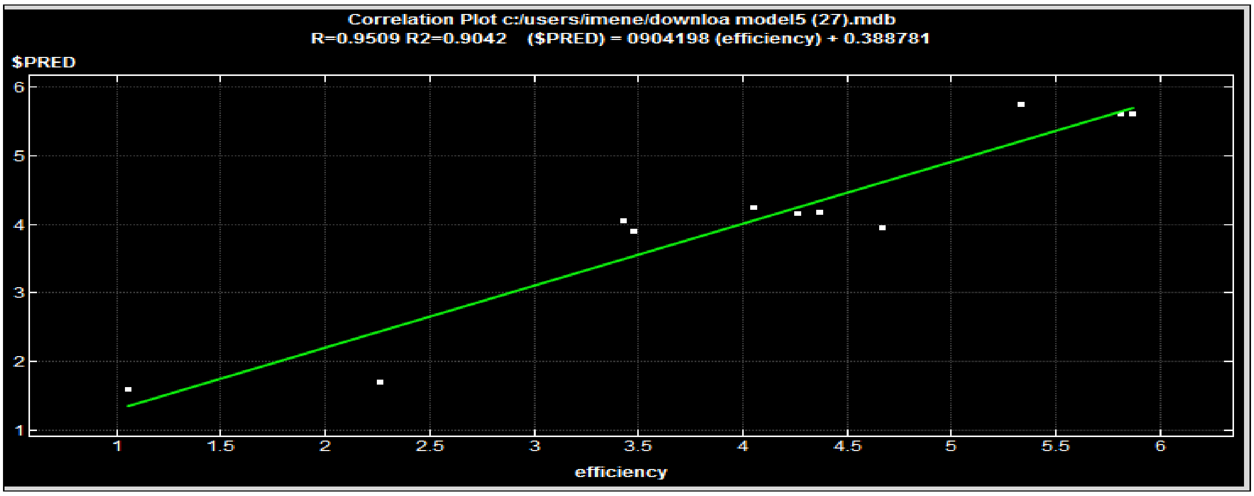


Figure IV-7: *Correlation of model 5.*

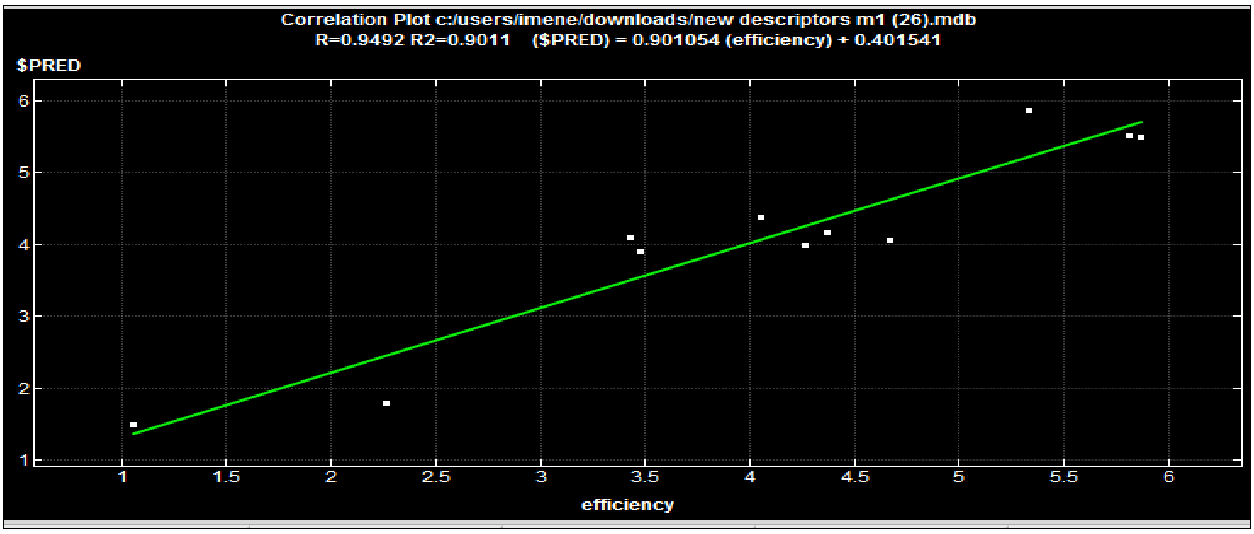
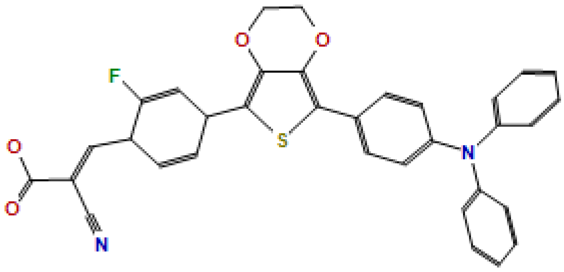
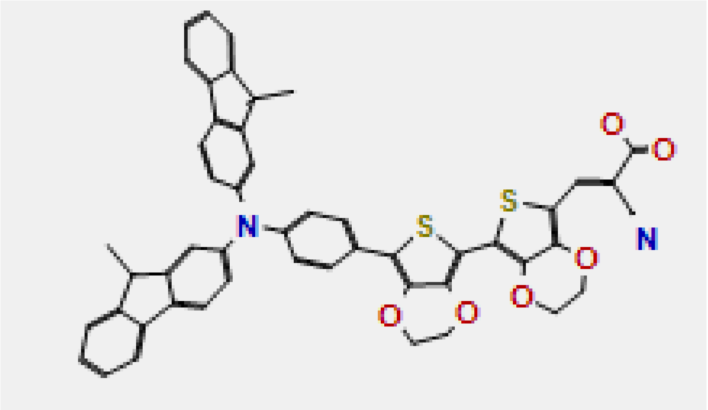
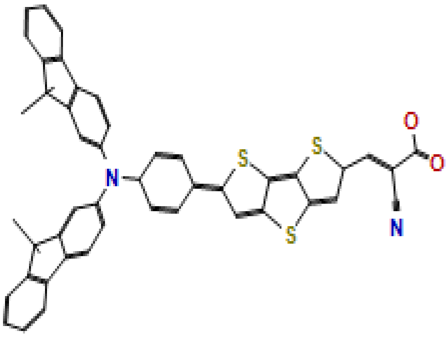


Figure IV-8: *Correlation of model 6.*

IV. 5. 2. *External validation*

- To evaluate the true and exact predictive power of the QSPR model, it is highly recommended to use an external test set with molecules that weren't used in the development of the model.
- After doing several tests using a set of 13 different molecules, we selected three molecules and used them to test the model number 3, the results are in the table below:

***Table IV-13**: external validation test results.*

	Moleculare structure	Efficiency PCE %	$PRED
1		5.0800	6.7015
2		6.2900	7.7304
3		8.0000	9.5746

- Explanations :
  - The power conversion efficiencies PCE of the three molecules predicted by the model are approximately close the experimental values (taken from the literature), as a result, robustness and stability of the model 3 are confirmed.
  - The plot of correlation between the observed efficiency of molecules and the calculated one is a confirmation of the predictiveness of the model.

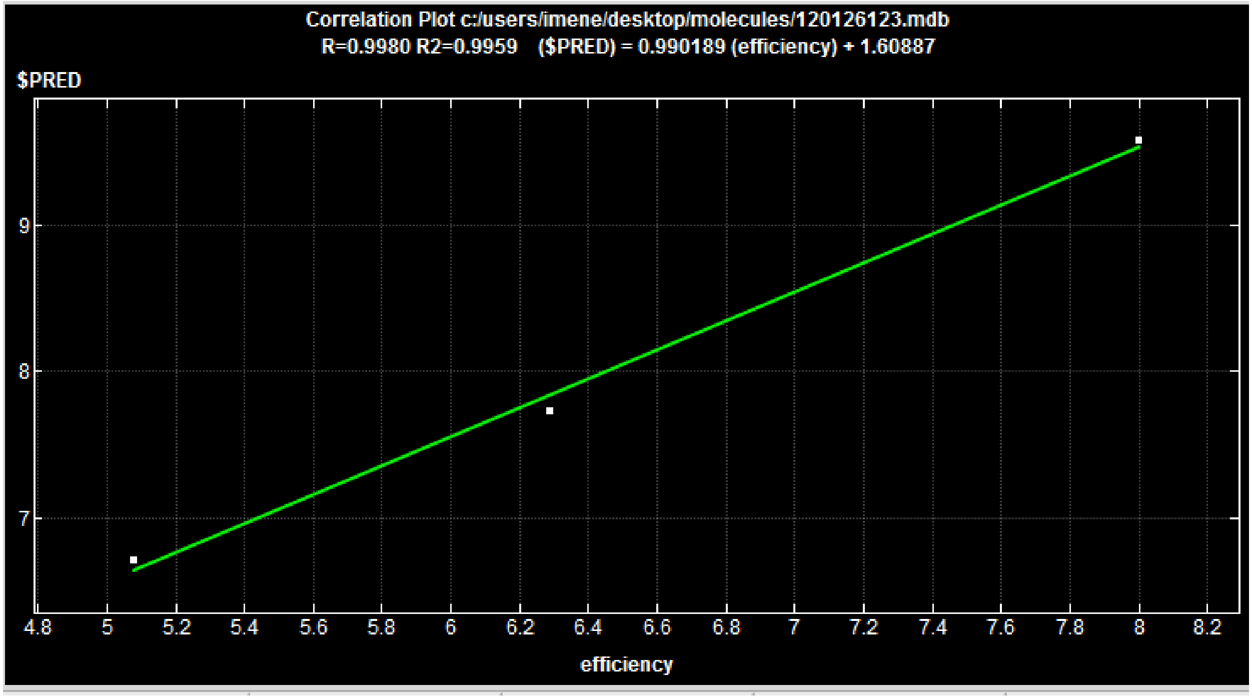


Figure IV-9: *Correlation between the QSPR model and the tested molecules.*

V. CONCLUSION

The QSPR models have been successfully developed. The one developed with these 3 significant descriptors: **b_1rotR, MNDO_LUMO, vsurf_DW13** showed a good correlative and predictive ability for predicting power conversion efficiency PCE and has been chosen as an accepted powerful model with cross-validation correlation coefficient of **0.74546** and root mean square error of **0.72634**, the effectiveness of this chosen model was also confirmed by the values of **ZSCORE** and **XZSCORE** that were generally less than **2.5** .This model demonstrated a high degree of accuracy, it was then validated after an external test set. The developed QSPR model can now be used to discover and confirm the power conversion efficiency of new sensitizers.

References

[1]: C. Fan, M. Springborg and Y. Feng, Phys. Chem. Chem. Phys., 2019, DOI: 10.1039/C8CP07722C.

[2]: A.F Buene and all" titled "A comprehensive experimental study of five fundamental phenothiazine geometries increasing the diversity of the phenothiazine dye class for dye-sensitized solar cells " published in the journal " ELSEVIER" in 2019.

GENERAL CONCLUSION

GENERAL CONCLUSION

The objective of this manuscript was to establish a QSPR model that can predict the power conversion efficiency of new sensitizers for dye sensitized solar cells. In a first part, we presented a general overview of photovoltaic conversion, starting with the operating principle and all the different types of cells to the economic aspects from cell's fabrication phase to electrical power generation. The production process of electrical power in large scale using classic photovoltaics is highly expensive, dye sensitized solar cells appears to be the perfect alternative solution in its application domain. In the second part, we detailed this organic-based solar cells, investigating all the different compounds that we can work on to improve its efficiency.

DSSCs have been attracting global attention since its first discovery in 1991 by GRATZL, because of its conversion efficiency, easy fabrication process and low manufacturing cost. Huge efforts have been devoted to the investigation of the outstanding dye sensitizers, to harvest more photon while maintaining high charge recombination resistance and also due to their unique advantages, for instance, convenient molecular design, tunable absorption, eco-friendliness, no resource limitation along with low synthetic and purification cost when compared with metal-complex sensitizers.

For this aim, we introduced in the third part of our work the QSPR modeling and quantum chemical methods used to build the predictive model. Density functional theory and time dependent are the important methods used. Understanding the basic electron transfer mechanism along with the structural attributes of organic dye sensitizers for the DSSCs explicit to liquid electrolyte allows to set up the quantitative relationship between the overall PCE and quantum chemical molecular descriptors calculated by the DFT (TD-DFT) integrated in the MOE software.

The last part of this manuscript was dedicated to the development of the QSPR model, we collected a set of data with experimental values of power conversion efficiency and used it to build our model. Among 124 descriptors in the Moe's library, we selected 6 descriptors that satisfied certain conditions, and used them to develop the QSPR models. Then the best model was validated.

This QSPR model enables prediction of essential molecular property attributes necessary to go forward in improving DSSCs efficiency. It could guide the design and synthesis of more efficient dyes in the near future.